CHARACTERIZATION OF VIRGIN AND HYDROGENATED LIQUIDS FROM SPOUTED BED PYROLYSIS OF CANADIAN COALS

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ABSTRACT

This report describes work carried out under the Contract OST 84-00151 DSS File: 24ST.23440-4-9074 to Canada Centre for Mineral and Energy Technology (CANMET) of the Department of Energy, Mines and Resources, Ottawa for the period from October 1985 to the end of May 1986.

Repeated rapid pyrolysis runs of bituminous Devco coal were conducted on a pilot scale spouted-bed unit at 665 ± 15°C and a feed rate of 0.7-1.2 kg/hr to produce three kilograms of raw tar. The middle-distillate fraction (110-390°C) was obtained from the raw tar via short-path vacuum distillation.

The middle-distillate was subjected to nine different hydrotreating experiments in which liquid feedrate, H_2-pressure, LHSV and temperature were explored at different levels. H_2 consumption is reported, as well as the elemental analysis for C, H, N, O and S in tar, tar distillates, residual coke and all the hydrotreated liquids. Detailed hydrocarbon group-type analysis was carried out for tar distillates and all hydrotreated samples using a combination of high resolution gas chromatography and gas chromatography-mass spectroscopic methods. Approximately 100 individual compounds were positively identified in each of the hydrotreated liquid samples. Compound classes identified included alkanes, substituted benzenes, cycloalkanes, naphthalenes, indans and their partially hydrogenated homologs. The extent of the removal of the heteroatomic species, such as phenols, quinolines and acridines from the original tar distillate during hydrotreating was established.

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1. INTRODUCTION

In the previous work (1) it was reported that the laboratory bench-scale continuous feed (30-60 g/h) spouted-bed pyrolyser is a useful means for conducting rapid-pyrolysis of Canadian coals. Forestburg, Sukunka and Devco coals were tested with extensive evaluation of the tar quality. In the present work the focus was put on the abundantly available Eastern Canadian Devco coal.

The detailed work statement for this contract is described in the contract DSS File: 24ST.23440-4-9074. In brief, the objective was to test Devco coal in a pilot scale spouted-bed pyrolyser with collection of the evolved tar liquid. The middle distillate (110-390°C) of this tar was to be used for hydrotreating experiments. The heteroatomic species in the raw tar and those which remained in the hydrotreated product were the main factors of interest. Detailed characterization was to be carried out, therefore on the raw tar and on the hydrotreated products.

Undoubtedly, the refining of coal derived liquids will require the modification of established processing steps now used in refining petroleum, as more severe conditions are in general required for non-conventional petroleum sources. Modifications are required because the chemical structure of the coal derived liquids is very much different from crude petroleum, being enriched in aromatic species and heteroatomic containing materials. Clearly, this will seriously affect the efficiency of the hydrotreating process. Furthermore, the quality of coal liquid depends on the parent coal and the process which the coal liquid was derived.

In the present report, the initial section outlines the pilot-scale rapid pyrolysis of Devco coal, with emphasis on the coal tar liquid recovery. The problems associated with the distillation of the heavy Devco tar are

also identified. The middle-distillate (110-390°C) obtained from the U.B.C. in-house distillation was subjected to catalytic hydrotreating experiments conducted by the Petroleum Division of Saskatchewan Research Council. The bulk of the report deals with the characterization of the original tar fractions and the hydrotreated middle distillates. The middle-distillates are highly complex mixtures of different group-type hydrocarbons including aliphatic, alicyclic, aromatic and heteroatomic (O, N and S) containing species. Hydrotreating experiments were carried out by the subcontractor under nine different process conditions. The hydrotreated liquids are less complex than the feedstock as a consequence of partial or extensive deoxygenation, denitrogenation and desulphurization.

Based on the previous work and experience on coal liquid characterization, all the hydrotreated liquid samples were evaluated in depth via high resolution gas chromatography and the gas chromatography-mass spectroscopic method.

2. PILOT SCALE SPOUTED-BED PYROLYSIS EXPERIMENT OF DEVCO COAL

2.1 System description and procedure for pyrolysis tests

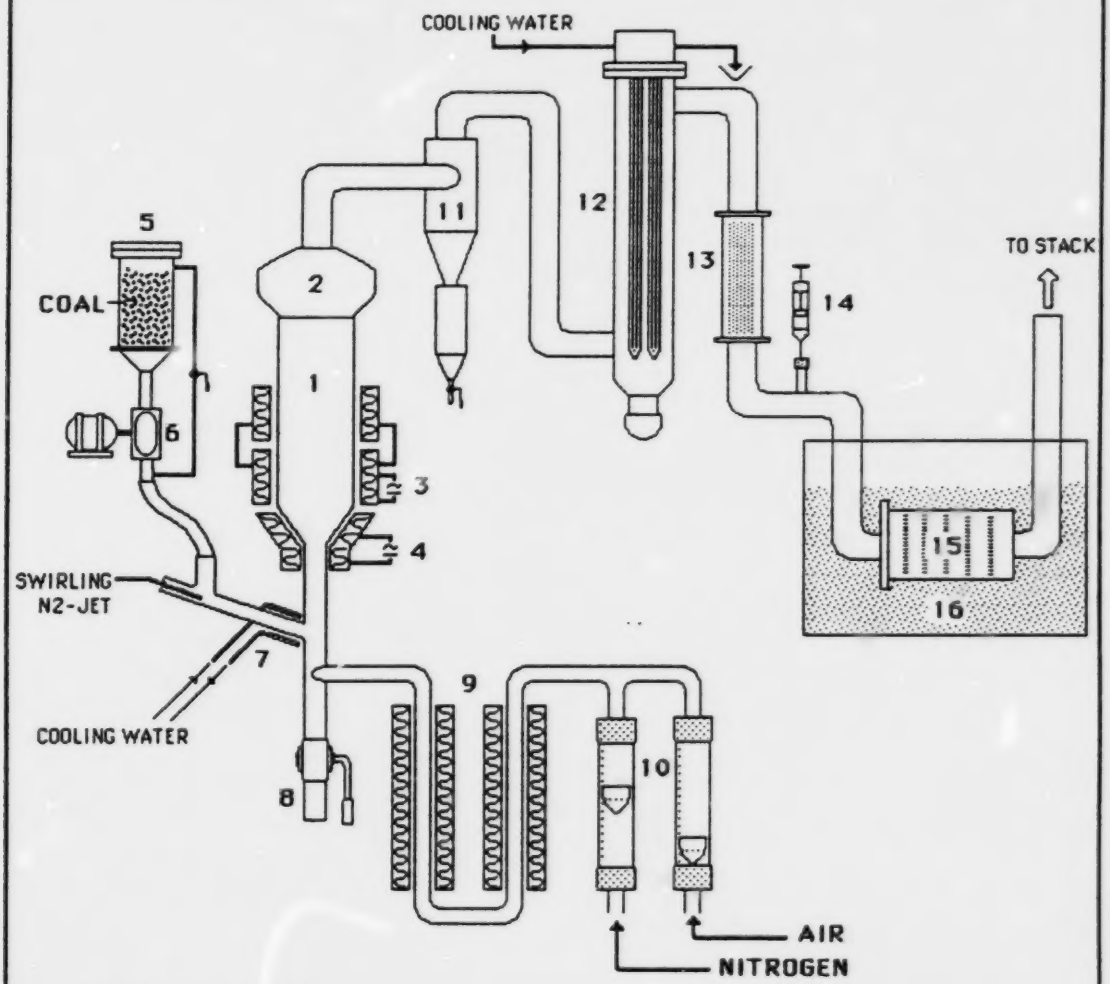
The pyrolysis unit used in all the experiments is shown in Figure 1. The physical details are collected in Table 1. The dual-stage gas preheater was electrically heated to maintain the spouted gas at an inlet temperature of about 650°C. It was estimated that the residence time for the coal particles in the spouted-bed inlet under the entrainment stream of preheated nitrogen gas is in the order of 10 millisecond.

Prior to the commencement of a pyrolysis run, preheated air was used to precondition the reactor and establish the spouting silica sand bed (cf. 4.0 - 4.5 kg/16 mesh) over a period of 2 hours. Once the bed reaches the desired temperature, the air stream was replaced by nitrogen gas. Ten minutes was allowed for replacement of air from the system and equilibration.

Coal (-1.7 + 0.7 mm) was fed from coal hopper via the rotary feeder. In order to achieve a smooth feed and minimize blockage, a swirling nitrogen jet was used. In addition, steps were taken to avoid prematurely heating the coal particles prior to the feed point, since at ca. 400°C a sticky meso-phase occurs readily for this highly caking coal. Therefore, the temperature of the coal conveying tube upstream of the feed junction was maintained below 250°C with the aid of an external cooling coil.

Tar vapor produced during the pyrolysis run was first quenched to ca. 70 to 80°C in the heat exchanger and partially condensed in the pyrex trap which was packed with stack of metal mesh to promote collection. Further tar condensation took place in the U-trap immersed in the ice-bath. Any remaining uncondensed materials, uncollected droplets and gases were carried

FIGURE 1 SCHEMATIC DIAGRAM OF THE SPOUTED BED PYROLYSER



1. SPOUTED BED REACTOR
2. DISENGAGEMENT SECTION
3. COLUMN HEATER
4. CONE HEATER
5. COAL HOPPER
6. STAR FEEDER
7. COOLING COIL
8. BED DRAIN
9. DUAL ELECTRICAL HEATERS
10. GAS ROTAMETERS
11. GAS-SOLID CYCLONE
12. HEAT EXCHANGER
13. PYREX TAR TRAP
14. GAS SYRINGE
15. U-SHAPED TAR TRAP
16. ICE-BATH

by K. C. TEO

TABLE 1: DESIGN CHARACTERISTICS OF ELECTRICALLY HEATED SPOUTED BED PYROLYSIS SYSTEM

Reactor:	Material - 317 stainless steel Inner diameter = 128 mm Wall thickness = 6.6 mm Cone angle = 70o Disengement section, diameter = 255 mm Height, cone and disengagement section = 1.22 m
Spouted Bed Inlet Orifice:	Material - 316 stainless steel Diameter of orifice = 19.1 mm
Gas-solid Cyclone:	Material - stainless steel Diameter = 150 mm Cyclinder height = 500 mm Cone height = 300 mm
Heat Exchanger:	Shell - 316 stainless steel Inner diameter = 150 mm Wall thickness = 6.6 mm 6 x U-tubes: length 0.86 m, diameter 12.7 mm, total area 0.41 m^2
Tar Traps:	First trap - 102 x length 305 mm QVF Pyrex column with concentric metal mesh filter Second trap - 200 x 450 mm stainless steel U-trap inner volume ≈ 17 liters, with mesh metal screen filters
Dual Stage Gas Preheater:	Two - 80 x 900 mm stainless steel columns, maximium ouput = 3 kw each
Compressed Air:	From building supply
Nitrogen Gas:	From liquid nitrogen tank Capicity 200 liters of liquid nitrogen

to the roof-top propane fired burner. Gas samples were taken at an interval of every 30 minutes for a typical run of 3 hours.

Char was collected by the cyclone as fines and partly as agglomerates with silica sand in the bed.

2.2 The Devco Coal

The Devco coal was kindly supplied directly from the Lingan Mine of Cape Breton Development Company, Nova Scotia. A sample of about 200 lbs of 2 inch lumps of cleaned and washed coal was received in two shipments. The received coal was crushed and screened to provide the desired particle size range (-1.7 + 0.7 mm) for the pyrolysis task. Proximate and ultimate analyses were conducted by Commercial Testing & Engineering Company of Vancouver, and the results summarized in Table 2. The proximate result indicates the coal has a volatile content of 36.2% which is characteristic for its high caking property (FSI = 7.5). The atomic H/C ratio derived from the ultimate analysis is 0.80 which is typical for bituminous coal.

2.3 Tar recovery procedure and handling

Due to the heavy nature of the Devco tar, condensation began downstream of the cyclone ducting and carried over as far as to the exit of the exhaust ducting upstream of the propane burner. The residence time for the cool tar gas in the U-trap (vol. 17 liters) is in the order of 4 seconds. It was later found that the recovered tar contains a low proportion of lower boiling fraction (IBP - 110°C). Perhaps, for these volatile components a 4 second residence time in the U-trap might be inadequate for cooling. In addition, the condensed tar liquid droplets are constantly subjected to the velocity of the gas stream. An electrostatic precipitator would be a useful addition.

TABLE 2

PROXIMATE AND ULTIMATE ANALYSIS OF DEVCO COAL AND CHAR

	Devco Coal	Blend Char[(a)]
Proximate Analysis (as received basis):		
Moisture	1.08	0.73
Ash	3.03	54.59
Volatile Matter	36.18	5.49
Fixed Carbon	59.17	39.19
Sulphur	1.38	0.62
FSI	7.5	0
Calorific Value, BTU/lb	14,879	6,153
Ultimate Analysis (dried basis):		
C	83.71	41.38
H	5.62	1.74
N	1.82	1.07
S	1.40	0.62
Cl	0.04	0.00
Ash	3.06	54.99
O(b)	4.35	0.20
Total	100.00	100.00

(a) Blend char sample from pyrolysis runs.
(b) Oxygen, by difference = 100% - (C + H + N + S + Cl + Ash)%

The tar was recovered by washing out all the tar containing surfaces, (such as the heat exchange tube bundle, ducting and trapping units) with tetrahydrofuran (THF) solvent. The THF wash was stored under a nitrogen blanket prior to solvent stripping. A total of about 5 liters of THF tar wash was collected from each pyrolysis run.

Solvent stripping was carried out on a flash rota-evaporator under reduced pressure (15 mm Hg) and at a bath temperature of ca. 55°C. The recovered tar was subsequently stored in a sealed container under a nitrogen blanket and kept in a freezer (≈-15°C).

The tar container was surrounded with vermiculite enclosed in a metal can, which in turn was repacked into a corrugated container. Direct shipping to Regina was handled through the Cargo Department of Air Canada at the Vancouver Airport. The tar was classified as "dangerous goods", under the coding of naphtha liquid with flash point higher than 60°C.

2.4 Pyrolysis runs conducted between November and December of 1985

Eight pyrolysis runs were conducted after modifications to the pyrolysis system for the coal feeding unit and the installation of two consecutive tar traps as described in Section 2.1. The pyrolysis results are collected in Table 3 together with the gas composition and product distribution. The two start-up runs failed primarily due to plugging in the feed-line. The failure of Run DT06 was due to the down-stream (cf. after the U-trap) exhaust blockage.

A total of 3.1 kg of tar was recovered from the five successful runs (DT03, 04, 05, 07 and 08) by the procedure as outlined in Section 2.3. The average recovery tar yield for all the five runs is estimated at 19.9% on coal fed basis. The overall tar recovery efficiency is estimated at ca. 69% (see Section 2.6).

The tar was shipped by air to Petroleum Division of Saskatchewan Research Council on 23 December, 1985.

2.5 Pyrolysis runs conducted between February and March 1986

A second batch of tar liquid of 2.8 kg was prepared under the same conditions as for the first batch (as stated in Section 2.4) from the pilot scale pyrolysis runs DT11, 12, 13, and 14. The product distribution and gas compositions are summarized in Table 4. The average recovered tar yield for all the four pyrolysis runs is estimated at 21.0% on a coal fed basis. The overall tar recovery efficiency is estimated at ca. 74% (cf. Section 2.6). The tar was subjected to in-house vacuum distillation to produce the required 1 liter quantity of middle-distillate (see Section 3).

2.6 Pyrolysis product distribution

Detailed product distribution in terms of gas, tar liquid and char are summarized in Tables 3 and 4.

(a) Gases: It was found that for pyrolysis Run DT07 and 08 (Table 3) CO_2 and/or CO were produced in considerable amount compared to other runs. The cause is unclear, but perhaps is a small air leak from the air supply line into the system or the presence of a higher oxygen concentration in the nitrogen supply. It was noted that for Runs DT07, 08, 13 and 14 (Tables 3 and 4) C_3^+ and higher hydrocarbon species were found in substantially higher and variable concentrations compared to those of hydrogen, methane, ethane and ethylene. This might be due to different degrees of condensation of these higher hydrocarbon at the port of gas sampling.

The average mole ratio of C_2H_4/C_2H_6 for all the 8 pyrolysis runs was found to be 0.60 ±0.16, this value is lower than the expected value of ca. 0.82 found in earlier studies (Figure 4-1, page 32, ref. 2).

TABLE 3

PILOT SCALE PYROLYSIS OF DEVCO COAL (Run No. DT03 to DT08)

Coal Particle Size = -1.7 + 0.7 mm
Spouted Bed Material: silica sand (16 mesh) = 4.53 kg
N_2 Spouting Velocity = 0.85 - 1.10 m/sec

Pyrolysis Run No.[a]	DT03	DT04[b]	DT05	DT07	DT08
Coal feed rate, kg/hr	0.66	1.23	1.20	1.21	1.21
Duration, hr.	1.5	3.0	3.0	3.0	3.0
Pyrolysis temp., °C	691	638	658	692	680
Gas Yield, %[c]					
Components					
H_2	0.09	0.10	0.06	0.10	N.A.
CH_4	1.35	1.67	1.74	1.98	0.24
C_2H_4	0.37	0.21	0.28	0.43	0.42
C_2H_6	0.80	0.59	0.54	0.71	0.55
C_2H_2	-	-	-	0.04	-
C_3H_8	1.82	0.81	0.69	1.32	1.36
C_4H_{10}	0.87	1.36	1.42	2.07	2.68
C_5H_{12}	0.50	0.67	0.67	1.91	2.16
CO	0.42	0.19	0.29	0.88	3.58
CO_2	0.62	0.37	0.75	2.10	5.13
Total Gas Yield, %	6.84	5.97	6.44	11.54	16.11
Normalized Yield, %					
Gas	6.5	7.2	7.2	12.7	16.1
Tar	19.3	13.5	25.6	25.0	23.6
Char	74.2	79.3	67.2	62.3	60.3
Closure, %	104.8	82.9	88.5	90.4	99.8

(a) Run No. DT01, 02 and 06, failed due to feeding & blockage problems.
(b) Substantial char buildup in bed.
(c) As received, N_2-free basis.

TABLE 4

PILOT SCALE PYROLYSIS OF DEVCO COAL (Run No. DT11 to DT14)

Coal Particle Size = -1.7 + 0.7 mm
Spouted Bed Material: silica sand (16 mesh) = 4.53 kg
N_2 Spouting Velocity = 0.85 - 1.10 m/sec

Pyrolysis Run No.[a]	DT11	DT12	DT13	DT14
Coal feed rate, kg/hr	0.83	0.91	0.82	1.06
Duration, hr.	3.0	2.75	5.0	3.83
Pyrolysis temp., °C	676	681	651	666
Gas Yield, %[b]				
Components				
H_2	0.07	0.07	0.14	0.20
CH_4	1.20	1.96	1.66	1.89
C_2H_4	0.32	0.46	0.67	0.28
C_2H_6	0.43	0.72	0.81	0.59
C_2H_2	-	-	0.35	--
C_3H_8	1.20	1.78	2.93	1.88
C_4H_{10}	1.29	1.37	4.47	3.03
C_5H_{12}	0.18	0.70	2.33	1.25
CO	0.74	0.58	0.89	0.96
CO_2	1.24	0.65	0.89	0.88
Total Gas Yield, %	6.67	7.59	15.14	10.96
Tar Yield, %[c]	26.2	29.7	21.3	26.3
Char Yield, %[b]	67.1	62.7	63.6	62.7

(a) Run no. DT10: 0.64 kg/hr at 677°C failed.
(b) Gas and char yield, as received basis.
(c) Tar yield, by difference = 100 - gas - char, %.

Acetylene was not found in most of the cases. The yields of hydrogen, methane, ethane and ethylene in the various runs were confined within their own narrow ranges. (b) Tar yield: From the previous 1984/85 bench scale evaluation on the rapid pyrolysis of Devco coal (1), the average observed tar yield is 26.0% at 650°C. This tar yield figure was obtained from the cryogenic recovery of total condensable tar components and assumed as 100% tar recovery. This 26.0% figure was used to estimate the overall recovery efficiency of tar for Tables 3 and 4 as follows:

(N.B. the recovered tar was found to contain ≈10% of THF solvent)

W, total coal feed = $\sum$(feed rate) x (duration), kg

Wr = weight of recovered tar, kg

RE, recovery efficiency = $[(0.90 \times Wr/W)/0.26] \times 100\%$

The overall results are presented in the following short Table A.

TABLE A

Origin	W, kg	Wr, kg	RE,%
TABLE 3	15.54	3.1	69
TABLE 4	13.15	2.8	74

The major losses from the tar yield as mentioned in Section 2.3 are attributed to the volatile components with boiling point ca. 120°C or lower.

(c) Char Yield: Due to the highly caking characteristics of the coal, even for a good successful pyrolysis run, char with enriched mineral component tends to build up gradually in the spouting bed as the pyrolysis progresses. Char aggregates and agglomerates with the bed sand would eventually change the spouting characteristics of the bed. From practical experience, it was found that gradual increases in the linear spouting velocity from an initial value of ≈0.85 to 1.10 m/s towards the end of the run would minimize the char build up and extend the duration of the run. The longest steady pyrolysis run conducted on this pyrolysis unit lasted 5 hours (cf. Run #DT 13). Undoubtedly, one of the essential advantages of the spouted-bed is that it provides a strong attrition action in the annulus to break up the char aggregates and char-sand agglomerates. Char yield from each run was derived from quantitative recovery of the char fines collected in the cyclone catch and the amount left in the bed.

A sample of blended char derived from all the runs in Table 4 was assayed for its volatile content (Table 2) and found to yield a residual amount of 5.5%. This indicates that depletion of volatile matter from the coal has proceeded to an extent of 80% or better, while the ash content is enriched from the 3% level in coal to 55% in the char. This high ash char still retains 41% of its calorific value. The atomic ratio of H/C is reduced from 0.8 in coal to 0.5 in the char.

3. DISTILLATION OF DEVCO COAL TAR

3.1 Tar distillation task conducted by sub-contractor: Petroleum Division of Saskatchewan Research Council (SRC)

The first batch of prepared Devco coal tar (3.1 kg) was received by SRC on January 6, 1986. They performed simulation distillation (SIMDIS) by gas chromatography on the CS_2 soluble fraction (see Appendix A) which indicated that the tar contained ≈35 vol % boiling in the range 160-396°C. The CS_2 solubles are shown to contain ≈55 vol % of 397 to 603°C boiling range species. Since CS_2 is not an appropriate solvent for Devco coal tar and in addition SIMDIS by GC for coal tar is also not appropriate for the aromatic rich coal tar, therefore these figures should be treated with caution.

The distillation of the coal tar was originally scheduled to be conducted under vacuum via short-path distillation or a wiped-film molecular still. Due to inadequate experience of SRC in handling the extremely heavy Devco coal tar, they attempted to have the coal tar distilled via spinning band distillation. The previous phase of work (1) indicated that spinning band distillation requires excessively prolonged heating periods (cf. 4-6 hours estimated for 500 ml tar) to accomplish the tar distillation. This will undoubtedly cause thermal degradation. In addition, higher boiling fractions always condense out at the cooler end of spinning band column and cause blockage at the port of collection. The tar sample sent to SRC was later transferred to a wiped-film evaporator (WFE) distillation unit. For an unclear reason, perhaps operational in nature and/or the WFE was not designed for heavy coal tar distillation, SRC was not able to perform the tar distillation. As a consequence, the 3.1 kg of tar was essentially destroyed over the period of the SRC handling.

3.2 Problems identified for heavy coal tar distillation

The boiling range of a hydrocarbon feedstock is one of its chief specifications, partly because diltillation is one of the principal processes used to separate one product from another. The unsuccessful distillation of the tar at SRC is attributed to substantial polymerization of the tar during transfer, storage and handling. The tar was shipped under nitrogen atmosphere.

Recently, M. F. Ali et. al. (3) have indicted that for successful wiped-film distillation of crude oil residues with boiling point up to 455, 535 and 675°C one needs to apply successively lower pressures and higher temperature in order to obtain the required distillation cuts. They also pointed out that it is essential to keep the distillation temperature below 300°C with 2 seconds or shorter residence time in the heated zone.

It is foreseeable that for coal tar distillation, it is likely to be more successful if conducted on a fresh tar sample. In practice, distillation heating to higher temperatures, say 200 to 300°C might be required due to the heavy nature of the tar. Thermal decomposition can be minimized if the duration at this temperature range can be reduced. In brief, for a successful distillation of heavy coal tar, such as the Devco tar, the following steps have to be taken:

(a) Conduct distillation on fresh tar sample

(b) Handle the tar under nitrogen atmosphere.

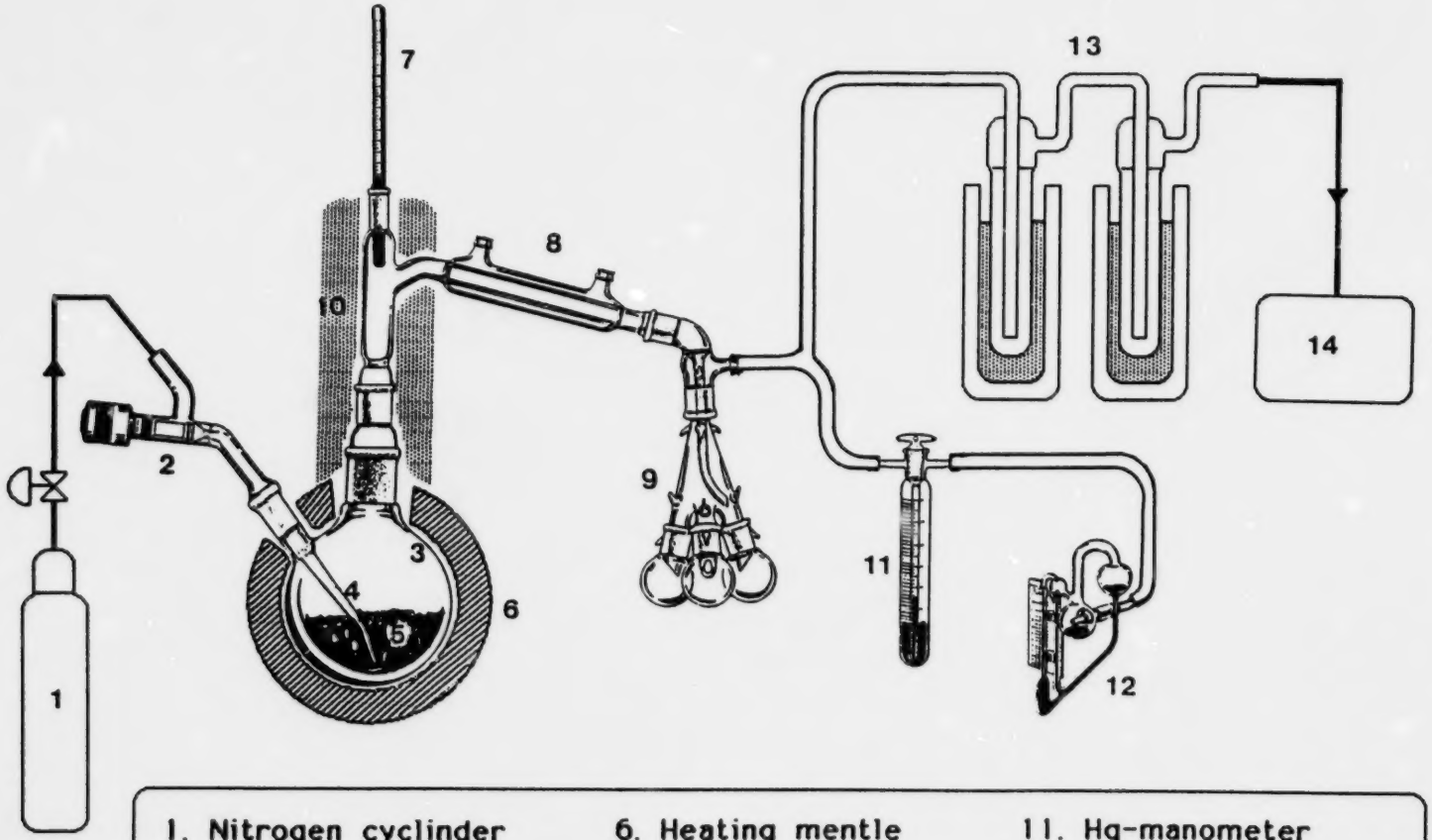
(c) Minimized the heating period of the tar.

(d) Avoid excessive heating to higher temperatures (cf. 300°C).

3.3 U.B.C. in-house tar distillation experiment

The experimental set-up is shown in Figure 2. About 470 to 610 g of fresh Devco Tar was used per distillation. A stream of nitrogen gas was bled

FIGURE 2 SHORT-PATH LENGTH TAR DISTILLATION



1. Nitrogen cyclinder	6. Heating mentle	11. Hg-manometer
2. Teflon vacuum valve	7. Thermometer	12. McLeod vacuum gage
3. 1-Litre flask, 2-necked	8. Air/water condenser	13. Liquid N2 traps
4. Drawn capillary	9. Distillation receiver	14. Vacuum pump
5. Coal tar liquid	10. Insulation	

through the heated tar liquid via a drawn capillary. The purpose of the nitrogen gas was to avoid bumping and to increase the rate of dynamic vapor saturation. The tar was first distilled at 30-40°C at 150 mm Hg to strip off the residual amount of THF solvent. Pressure was further reduced to 100-120 mm Hg with temperature increases to 50-60°C. The collected distillate was labelled as IBP-110°C. Distillation temperature was gradually raised to a final temperature of ca. 230-250°C with pressure at the proximity of 4-8 mm Hg. The bleed-through nitrogen gas stream was reduced accordingly in order to maintain the desired reduced pressure of the distillation system. Typical distillation time span is 1.5-2.0 hours.

Five distillations were accomplished at the rate of one distillation per day for the total 2.8 kg raw tar.

3.4 Product distribution and material balance

The overall product distribution in terms of the two boiling ranges and the residual formed coke is summarized in Table 5. The amount of first distillate with approximate boiling range IBP-110°C was low at 2.6%. This is primarily due to the lower recovery of the raw tar from the pyrolysis experiments (see Section 2.6).

TABLE 5

DEVCO COAL TAR DISTILLATION PRODUCT DISTRIBUTION

Distillate Fraction	Boiling range, °C	Weight %	Weight % THF-H_2O free basis
THF	67	14.3	-
water	100	~12	-
#1	IBP-110	1.8	2.6
#2	110-390	43.0	62.1
Formed coke	-	24.4	35.3
	Closure	95.5%	100.0%

TABLE 6

ELEMENTAL ANALYSIS OF DEVCO TAR AND DISTILLATES

SAMPLE	Elemental composition, weight%					
	C	H	N[b]	S	O[c]	Total[d]
Whole tar[a]	84.06	7.96	1.33	0.90	7.07 (6.65)	101.32
Distillate Fr #1 (IBP-110°C)	73.90	9.11	0.73	5.63	8.51 (10.63)	97.88
Distillate Fr #2 (110-390°C)	84.80	7.96	1.41	0.35	5.92 (5.83)	100.44
Coke from Distillation	88.11	4.34	2.25	0.39	4.60 (5.30)	99.69

(a) Tar sample without contamination of THF solvent.
(b) Nitrogen content less than 0.3% cannot be determined.
(c) Experimentally determined, accuracy ca (Value ± 0.50)%; value in parenthesis by difference = 100 - C - H - N, %
(d) Total = (C + H + N + S + O), %

The distillate fractions #1, 2 and the formed coke were assayed for their elemental composition C, H, N, S and O (Table 6). It was noted that although distillate fraction #1 has a higher H/C mole ratio 1.47 than that of fraction #2, H/C = 1.12, yet the accumulation of sulphur and oxygen are relatively high. The formed coke also is more enriched in nitrogen and depleted in hydrogen content as compared to the tar sample without the contamination of THF solvent and moisture.

Material balance for the tar distillation products in terms of the composite elements C, H, N, S and O are summarized in Table 7.

TABLE 7

ELEMENTAL BALANCE FOR TAR DISTILLATION PRODUCTS

Distillation product	Weight % (a)	Elemental contribution, %				
		C	H	N	S	O
Fraction #1	2.6	1.92	0.24	0.02	0.15	0.22
Fraction #2	62.1	52.66	4.94	0.88	0.22	3.68
Formed coke	35.3	31.10	1.53	0.79	0.51	1.62
Summation	100.0	85.68	6.71	1.69	0.88	5.52
		(C + H + N + S + O) = 100.1%				
Whole tar(a)	101.32	84.06	7.96	1.33	0.90	7.07

(a) From Table 5.

There are discrepancies in the elemental balance for H, S and oxygen. It is speculated that thermal decompositon might play an important role, in which case the depletion of hydrogen and oxygen contents might have taken the path via elimination processes to produce water, free hydrogen and/or lower hydrocarbon species. Undoubtedly, the distillation fraction #2 has a close resemblance in elemental composition to that of the original raw tar.

4. HYDROTREATING OF DEVCO TAR DISTILLATE FRACTION #2

4.1 Outline of the general approach used by SRC

The methodology proposed by the Petroleum Division of SRC for the hydrotreating of the Devco coal tar distillate fraction #2 is outlined in the following tasks. The process flow sheet is shown in Figure 3.

Task 1: Pilot plant presulphiding procedure

Catalyst: Shell S-424 (a commercial Ni-Mo hydrotreating catalyst)

Feedstock: Suncor gas oil containing 2.5% CS_2

Presulphiding the catalyst is necessary because commercial hydrotreating catalysts are manufactured and supplied in the oxide form. Therefore for optimum catalyst activity the metal oxidation the catalyst surface must be converted to the highly active metal sulphides. This is done by hydrotreating a gas oil (boiling range: 345 - 525°C) spiking with 2.5 wt.% of CS_2. The CS_2 is used as the sulphiding agent because it will decompose at a relatively low temperature and milder conditions. The details of the presulphiding treatment prior to the tar distillate hydrotreating experiments is described in Appendix B.

Task 2: Unit operation

The pressure specification for each hydrotreating experiment is the reactor pressure. It is equivalent to the hydrogen partial pressure at the reactor inlet because pure hydrogen is mixed with the liquid feed. The temperature is measured at approximately two thirds of the catalyst bed length in the reactor. The Liquid Hourly Space Velocity (LHSV) is a measure of the liquid feed rate and residence time in the reactor. It is defined as:

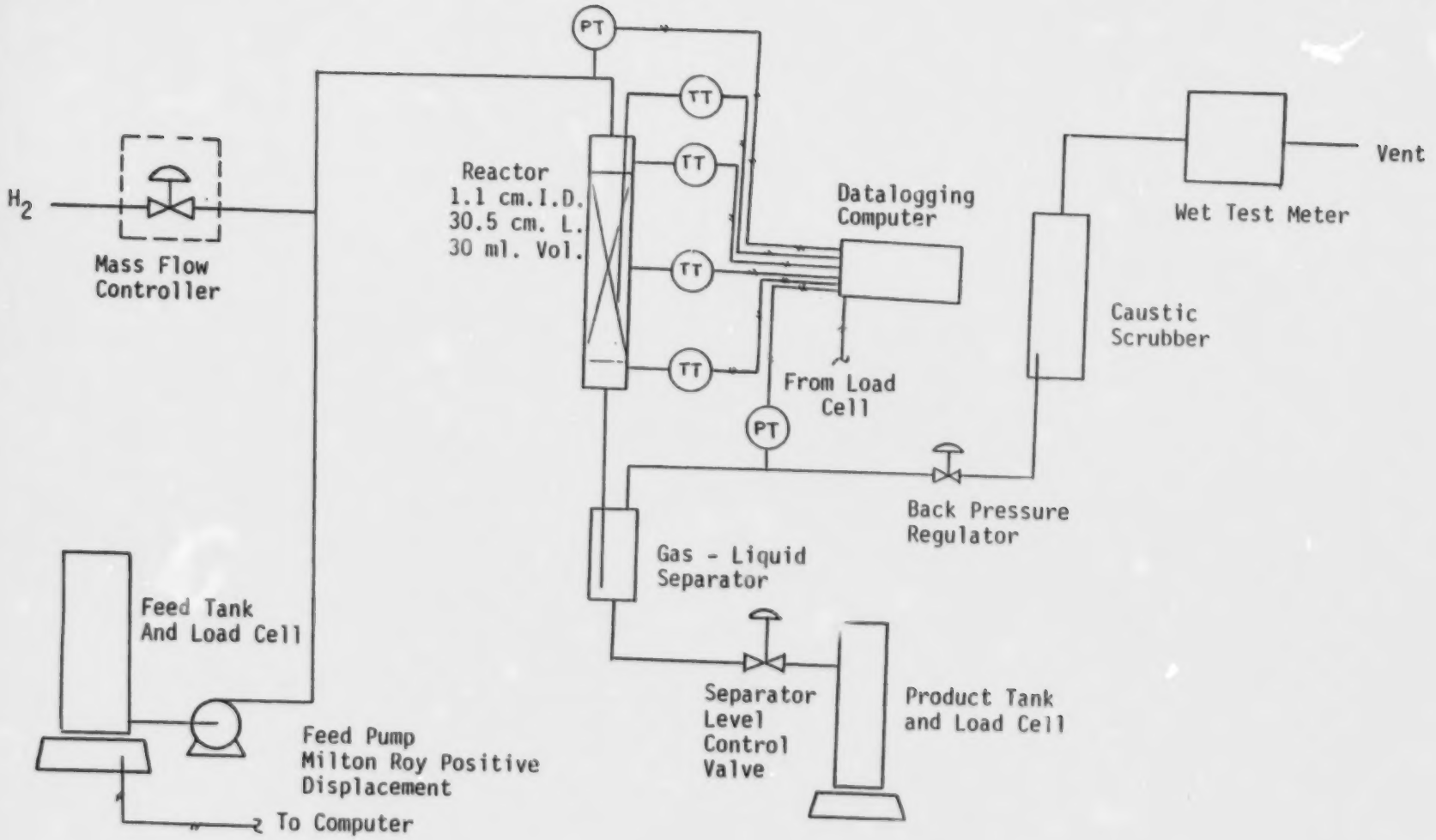


FIGURE 3 SCHEMATIC OF BENCH SCALE HYDROTREATING/HYDROCRACKING UNIT

LHSV = (Volume of feed/Time)/Volume of empty reactor, hr^{-1}

For the SRC bench scale unit: Volume of empty reactor = 30 ml

The above LHSV expression can be written as

$$\text{LHSV} = \frac{\text{Feed Rate (g/hr)}}{\text{Density @ 15°C(g/ml) x 30 ml}}$$

The density of the Devco tar distillate fraction #2 is determined to be 0.95 g/ml.

In commercial operation an ample excess of hydrogen is commonly used in hydrotreating processes, therefore a similar approach was used in this study. This is generally specified in terms of the liquid feed rate as,

$$\frac{\text{Volume of Hydrogen (at 15°C, 1 atm.), } m^3}{\text{Volume of Liquid Feed, } m^3}$$

In this study, each experiment is scheduled for a 4 hour continuous operation of which one hour is required to establish steady state and the severity of the hydrotreating conditions is selected from more severe conditions to the least severe one in terms of hydrogen pressure, reactor temperature and LHSV. A gas sample was collected and analysed for each 4 hour period.

Task 3: Data Management (see Appendix B)

The data is presented in terms of each set of operating conditions for

(a) hydrotreated liquid yield,

(b) hydrogen consumption,

(c) gas yield and gas composition

4.2 Summary and comparison of the various hydrotreating experiments

Nine hydrotreating experiments (SRC series #F86, Run 06C to 06J) were conducted for the middle distillate (fraction #2, 110-390°C). Each hydrotreating experiment is summarized in detail for mass balance, gas composition, product yield, operating conditions and operating anomalies that may impact on the liquid qualities. The nine hydrotreated liquid samples were received in good order on May 2, followed by the full report from SRC on May 20, 1986 (see Appendix B for the detailed report).

A condensed summary based on the detailed SRC report is collected in Table 8. The normalized gas compositions from the respective hydrotreating experiments, except 06G, are summarized in Table 9. The first five experiments, namely the 06A to E corresponding to higher severity in terms of hydrogen pressure (cf. 17.7 - 18.1 MPa) as compared to the rest. High reactor temperature, high H_2 pressure and low LHSV are considered as severe conditions. The approximate order of the severity is

$$06B > 06E \approx 06F > 06C \approx 06D \gg 06J > 06I > 06G \approx 06H$$

$$\text{Severity} \longrightarrow \text{decreases}$$

It was generally observed that at lower hydrogen pressure (< 7 MPa) the hydrotreating unit tends to have serious plugging problems and can not operate smoothly and uneventfully. The major cause was found due to the polymer formation and precipitation of ammonium salts in the reactor. The borderline conditions are clearly indicated from experiment 06J operating at a hydrogen pressure of 10.5 MPa. The possibility of rapid catalyst de-activation exists during the course of these experiments. A statement from the subcontractor is included in Appendix B concerning de-activation.

TABLE 8

SUMMARY ON THE HYDROTREATING EXPERIMENT OF DEVCO TAR DISTILLATE

	Hydrotreating Experiment No.[a]								
A. Reactor Conditions	6B	6C	6D	6E	6F	6G	6H	6I	6J
1. Temperature, °C	360	360	380	360	380	360	360	380	360
2. Pressure, MPa	17.9	18.0	17.7	17.9	18.1	7.2	6.8	10.8	10.5
3. Liquid Feed rate, g/hr.	10.5	28.0	29.0	12.0	14.0	25.3	31.25	16.75	15.25
4. Hydrogen rate, ml/min.	250	500	500	250	250	500	500	250	250
5. Duration, hr.	4	4	4	4	4	2.25	4	4	4
6. LHSV, hr^{-1}	0.37	0.98	1.02	0.42	0.49	0.89	1.10	0.59	0.54
B. Mass Balance									
1. Liquid Feed, g	42	112	116	48	56	57	127	67	61
2. Liquid Product, g	41.3	111.0	106.8	44.6	51.4	64.4	127.7	60.2	53.0
3. Liquid Yield, wt%	98.3	99.1	92.1	92.9	91.8	113.0	102.1	89.9	86.9
4. Gas vol., ℓ(15°C/1 atm)	15.2	43.4	52.86	25.0	22.5	55	80.7	22.2	39.3
5. H_2 consumption, g-mole/g-feed	0.0459	0.0295	0.0263	0.0345	0.030	(b)	0.014	0.025	0.0165
6. Gas yield (H_2 free) wt% fresh feed	2.75	2.67	5.94	10.6	5.2	(b)	3.4	5.6	14.2
C. Comment on the Hydrotreating Expt.	fair	stable	stable	stable	stable	un-stable see (b)	un-stable see (b)	stable minor prob-lem	stable minor prob-lem

(a) Saskatchewan Research Council, Petroleum Division, series no. F86
(b) Plugging in the hydrotreating system due to polymeric materials and ammonium salts, data not available.

TABLE 9

NORMALIZED GAS COMPOSITION FROM HYDROTREATING

Experiment No.[(a)]	Normalized Milli-mole Fraction, air free basis							
Components	6B	6C	6D	6E	6F	6H	6I	6J
Hydrogen	941.7	960.6	905.8	831.6	898.7	981.9	908.9	916.6
Methane	26.5	10.0	28.1	50.6	45.7	1.4	27.3	8.8
Ethane	7.1	4.9	11.1	17.3	16.8	1.3	11.9	5.0
Propane	2.6	6.4	11.3	14.9	16.1	1.8	11.8	6.7
i-Butane	0.9	0.7	1.0	1.2	1.3	-	1.2	1.9
n-Butane	7.5	9.6	10.5	10.1	1.2	6.8	13.6	14.3
i-Pentane	0.5	0.2	0.3	0.5	0.5	-	0.6	0.7
n-Pentane	0.4	0.3	0.5	0.8	0.7	-	1.5	1.0
C_6^+	1.5	3.2	3.0	-	-	-	16.1	38.4
Carbon dioxide	-	Trace	0.2	Trace	-	1.1	0.5	0.6
Carbon monoxide	-	0.4	0.6	0.3	0.6	1.2	1.3	1.7
H_2S	4.9	0.9	0.7	0.3	0.3	-	1.7	2.3
N_2 (or O_2*)	6.3	2.8	27.0	72.5	7.3	4.5*	3.6	2.0

(a) Not available for experiment no. 6G.

4.3 Correlation of elemental compositions of hydrogreated liquids with the hydroprocessing parameters

Catalytic hydrotreating of coal derived liquids should be given the greatest attention for the removal of heteroatoms, particularly oxygen, nitrogen, and sulphur. Since there are more serious problems on the severe poisoning effect of nitrogen containing species on the hydrotreating catalysts than by the oxygen and sulphur containing species, the removal of nitrogen bearing species is generally more difficult than the oxygen and sulphur.

Table 10 shows the elemental composition of the hydrotreating liquid samples. The table also indicates the extent to which hydrogen content can be added and the extent oxygen, nitrogen and sulphur can be removed from the middle tar distillate by the hydrotreating process. Under higher hydrotreating pressure (cf. 17.7 - 18.1 MPa for Runs 06B to 06F) oxygen and sulphur were reduced to <0.1% from 5.92% and 0.35% respectively, whereas nitrogen was reduced to below 0.3% from a value of 1.41%. At lower hydrotreating pressure (cf. 10.5 MPa) the residual nitrogen and oxygen remain high at 0.5-1% and 1.8-3% respectively. Undoubtedly, the liquid products from Runs 06G to 06J would require further denitrogenation and deoxygenation.

Figures 4 and 5 show the most significant characteristics of the hydrogen, oxygen and nitrogen contents in the hydrotreated liquids versus the actual H_2 consumption in each experiment. Higher H_2 consumption is always accompanied with a liquid product enriched in hydrogen content and reduced in oxygen and nitrogen contents. Since the H_2 consumption is a function of hydrotreating pressure, LHSV, H_2 recycling rate and temperature, therefore, a good way to evaluate the severity of a hydrotreating process is to correlate

the H_2 consumption with the elemental compositions of H, O and N of the resulting liquid products. Sulphur content did not give as smooth a correlation. Runs 6B and 6F had abnormally high sulphur contents compared to the trend through the data points of the other runs.

TABLE 10

ELEMENTAL ANALYSIS OF VIRGIN TAR FRACTION AND HYDROTREATED SAMPLES

HYDROTREATED SAMPLE (Series #F86)	Elemental composition, weight%					
	C	H	N[a]	S	O[b]	Total[c]
FRACTION #2 (d)	84.80	7.96	1.41	0.35	5.92	100.44
B	86.65	13.23	<0.3	0.06	(~0.0)	-
C	88.57	11.11	<0.3	0.03	(~0.0)	-
D	88.74	11.09	<0.3	0.02	(~0.0)	-
E	88.70	11.30	<0.3	0.01	(~0.0)	-
F	88.16	11.37	<0.3	0.06	(~0.11)	-
G	87.54	9.16	0.99	0.07	2.61 (2.24)	100.37
H	87.20	9.23	0.69	0.09	3.07 (2.79)	100.28
I	89.28	10.23	0.49	0.04	<.2 (0.00)	100.24
J	88.88	9.73	0.48	0.05	1.83 (0.86)	100.97

(a) Nitrogen content less than 0.3% cannot be determined.
(b) Experimentally determined, accuracy ca (Value ± 0.50)%; value in parenthesis by difference = 100 - C - H - N, %
(c) Total = (C + H + N + S + O), %
(d) From Table 6, page 18.

FIGURE 4 HYDROGEN AND OXYGEN CONTENTS OF HYDROTREATED LIQUIDS

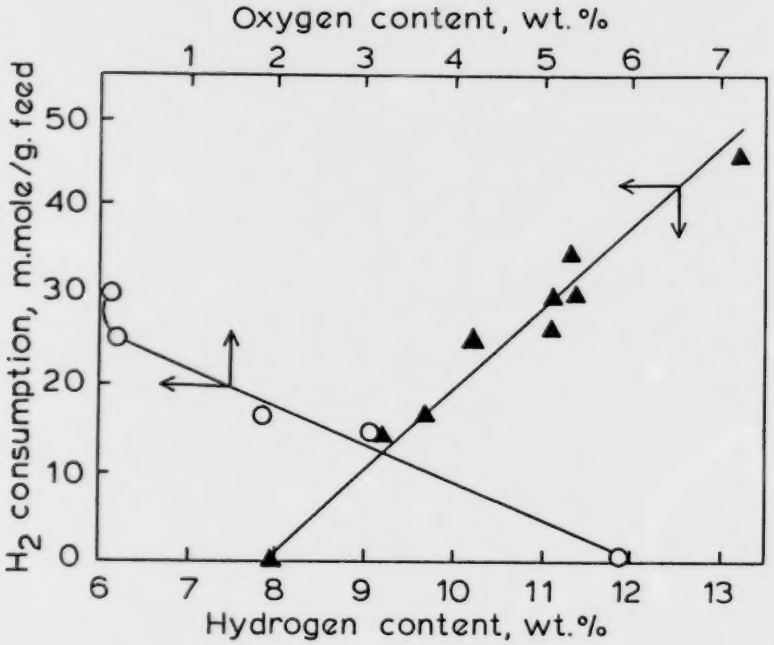
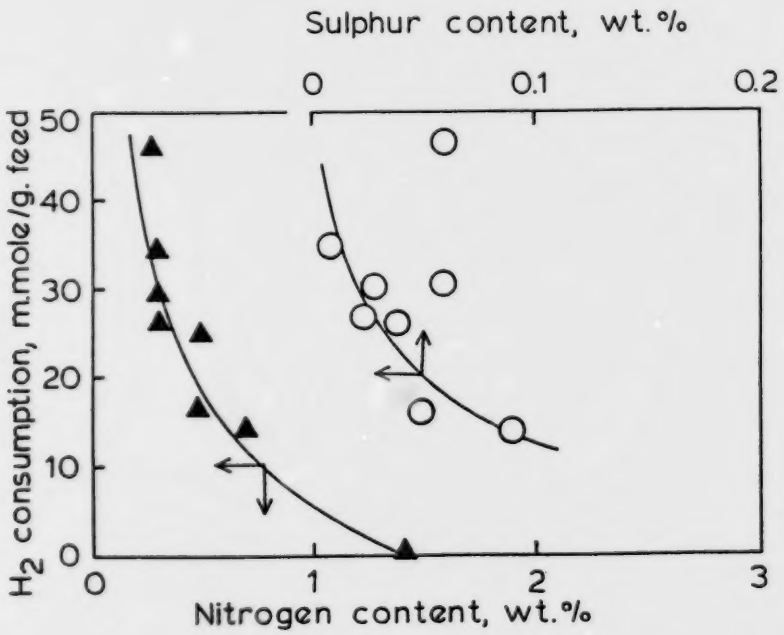


FIGURE 5 NITROGEN AND SULPHUR CONTENTS OF HYDROTREATED LIQUIDS



5. DETAILED CHEMICAL CHARACTERIZATION STUDY

5.1 The GC-MS and HRGC methods

Development of gas chromatography-mass spectroscopy (GC-MS) and capillary high resolution gas chromatography (HRGC) methods for detailed characterization of coal liquid products was the major task in previous contracts (1,2). Detailed knowledge of the composition of coal pyrolysis tar liquids and their distillates is important in evaluating down stream upgrading processes, such as catalytic hydrotreating.

Pyrolysis coal tar liquids, despite severe bond-breaking in the pyrolysis process, are highly complex mixtures of widely different compounds. In previous studies (1,2) Devco coal tar was shown to be a highly complex mixture containing aliphatic hydrocarbon (up to C_{29}^{+}), and dominated by aromatic hydrocarbons (1 to 5-ring), minor in phenols and N-heterocycles (2 to 4-ring) and traces of benzo-/dibenzo-thiophenes. In this study the same GC-MS and HRGC approach and methodology were used in evaluating the Devco tar distillates and the nine hydrotreated liquid products.

The experimental conditions for analysing the two tar distillates and the nine hydrotreated liquids by the HRGC and GC-MS are summarized below.

HRGC: (a) Varian Vista 6400 GC equipped with flame ionization detector and data station Vista 401 was used.

(b) GC operating conditions: DB5 capillary column (30 meters), argon carrier gas at 30 ml/min.

(c) Temperature programming: 50°C (isothermal 2 min.), heating rate at 5°C/min. to 300°C (hold for 28 min).

GC-MS: (a) Hewlett Packard 5845B GC-MS system, completed with data system and search libery.

(b) GC conditions: DB5 capillary column (28 meters), temperature programming 30°C (isothermal, 1 min), to 60°C (at 5°C/min), then to 290°C (at 8°C/min); carrier gas helium.

(c) MS conditions: quadrapole, electron impact mode, ionization potential 70 eV; mass range m/e 38-490 amu/scan rate 0.6 s.

Integration of the retention index approach to the HRGC as described in the previous report (2), and in conjunction with GC-MS study provides the detailed and positive confirmation of the GC peak assignments. For the present report some progress has been made to include the saturate alicyclic hydrocarbons (i.e. naphthenes), in particular the cyclohexanes, indans, tetra- and octa-hydronaphthalenes.

5.2 Characterization of Distillate Fractions #1 and 2

Details of the major individual compound homologs identified for the Devco tar distillate fractions #1 and 2 are collected in Table 11.

The HRGC and GC-MS traces of the distillate fraction #1 and presented in Figure 6 and 7A respectively, combined results from the two methods shown to contain 80 GC peaks. The detailed characterization is collected in Table 12. The results show that the fraction #1 contains an abundance of alkylbenzenes, n-alkane/1-alkene pairs (C_{11}-C_{18}), phenols, naphthalenes, and minor amounts of alkyl-sustituted quinolines, indoles, carbazoles, and traces of benzofurans, dibenzofurancs, fluorenes and unsubstituted phenanthrene. Selective ion monitoring (SIM) traces (Figure 7B) revealed the presence of the above mentioned homologous series. Hydrocarbon and derivative group

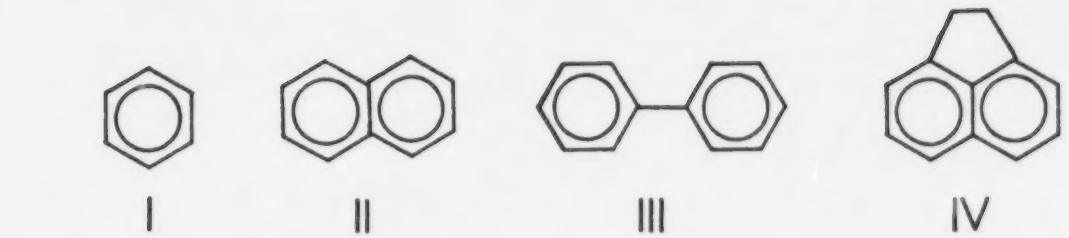
TABLE 11

POLYNUCLEAR AROMATIC HYDROCARBONS AND N, O, S-HETEROCYCLIC POLYNUCLEAR AROMATICS AND THEIR ALKYL DERIVATIVES FOUND IN DISTILLATE FRACTIONS

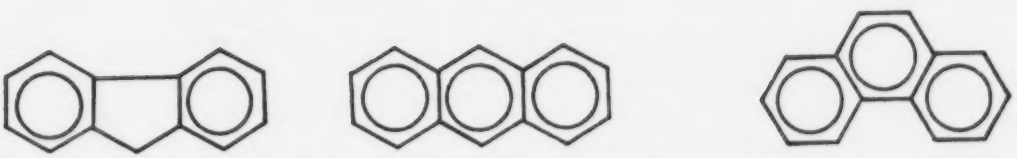
Molecular[(a)] Structure	Compound Class/Type	Molecular Formula of Parent Compound	Molecular Weight of Alkyl Substitution					
			nil	C_1	C_2	C_3	C_4	C_5
I	Benzene	C_6H_6	78	92	106	120	134	148
II	Naphthalene	$C_{10}H_8$	128	142	156	170	184	198
III	Biphenyl	$C_{12}H_{10}$	154	168	182	196	-	-
IV	Acenaphthene	$C_{12}H_{10}$	154	168	182	-	-	-
V	Fluorene	$C_{13}H_{10}$	166	180	194	208	-	-
VI	Anthracene	$C_{14}H_{10}$	178	192	206	220	-	-
VII	Phenanthrene	$C_{14}H_{10}$	178	192	206	220	-	-
VIII	Fluoranthene	$C_{16}H_{10}$	202	216	230	-	-	-
IX	Pyrene	$C_{16}H_{10}$	202	-	-	-	-	-
X	Benzofuran	C_8H_6O	118	132	146	160	-	-
XI	Dibenzofuran	$C_{12}H_8O_8$	168	182	196	210	-	-
XII	Indole	C_8HN	117	131	145	159	-	-
XIII	Carbazole	$C_{12}H_9N$	167	181	195	209	-	-
XIV	Quinoline	C_9HN	129	143	157	-	-	-
XV	Acridine	$C_{13}H_9N$	179	193	207	221	-	-
XVI	Benz[b]-thiophene	C_8H_6S	134	148	162	-	-	-

(a) On the following page.

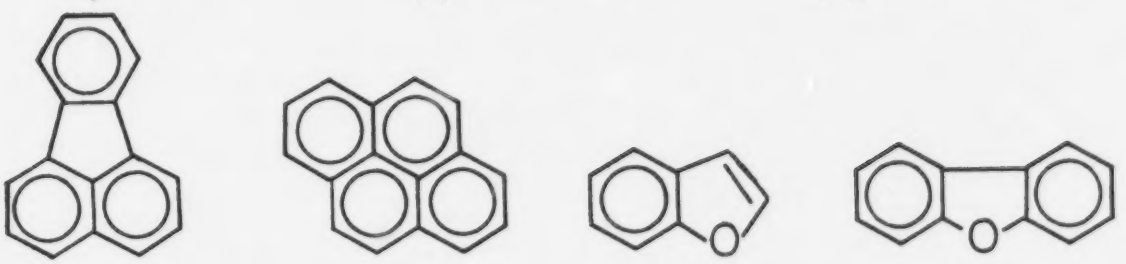
TABLE 11 (continued)



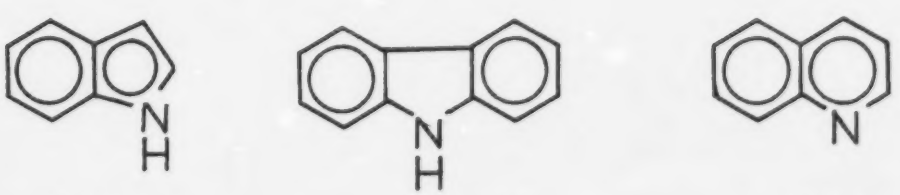
I II III IV



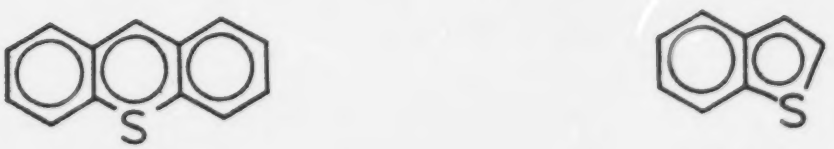
V VI VII



VIII XIX X XI



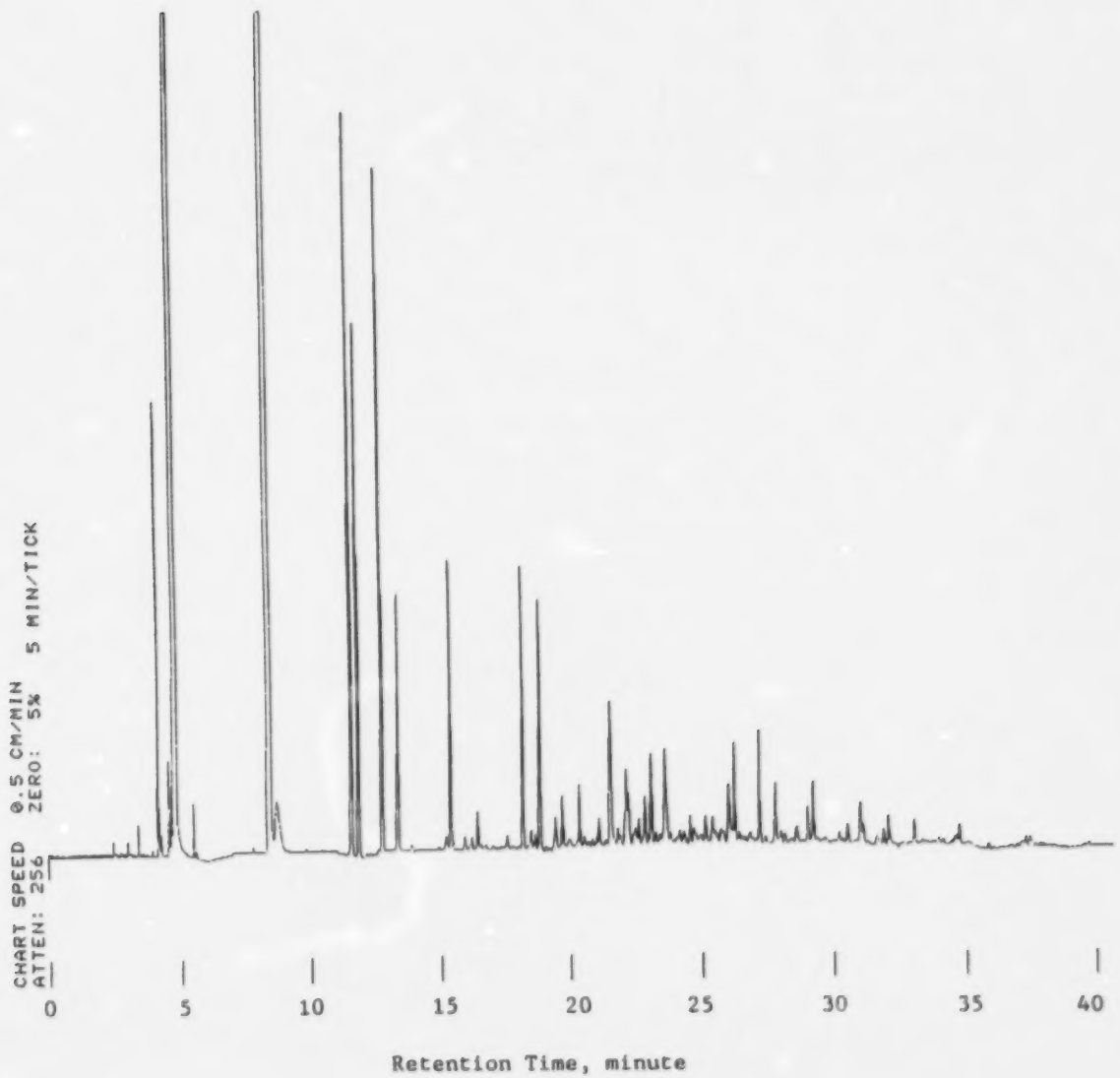
XII XIII XIV



XV XVI

FIGURE 6

HRGC OUTPUT OF DISTILLATE FRACTION #1



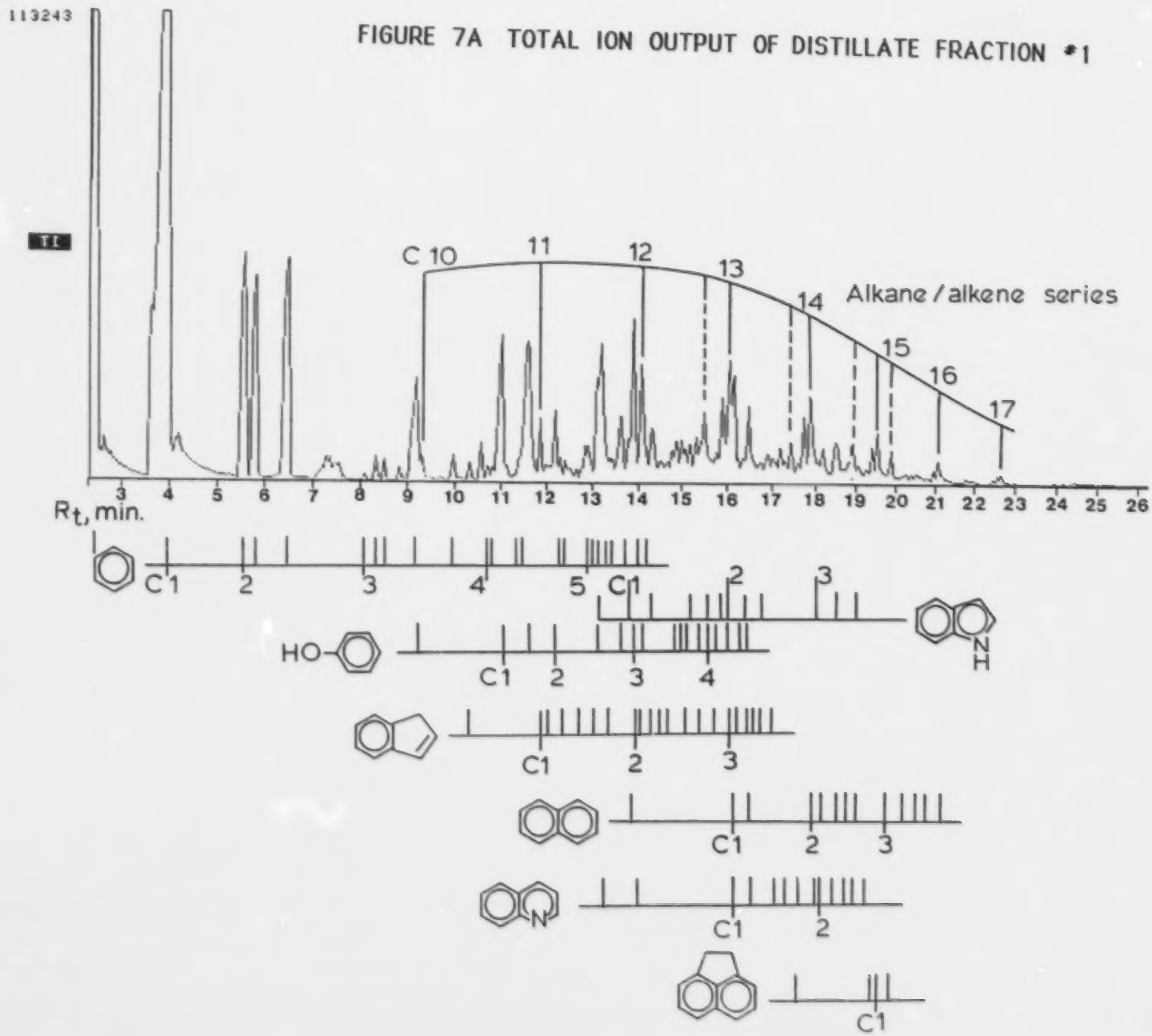


FIGURE 7A TOTAL ION OUTPUT OF DISTILLATE FRACTION #1

FIGURE 7B SELECTIVE ION MONITORING OF DEVCO COAL TAR DISTILLATE FRACTION #1

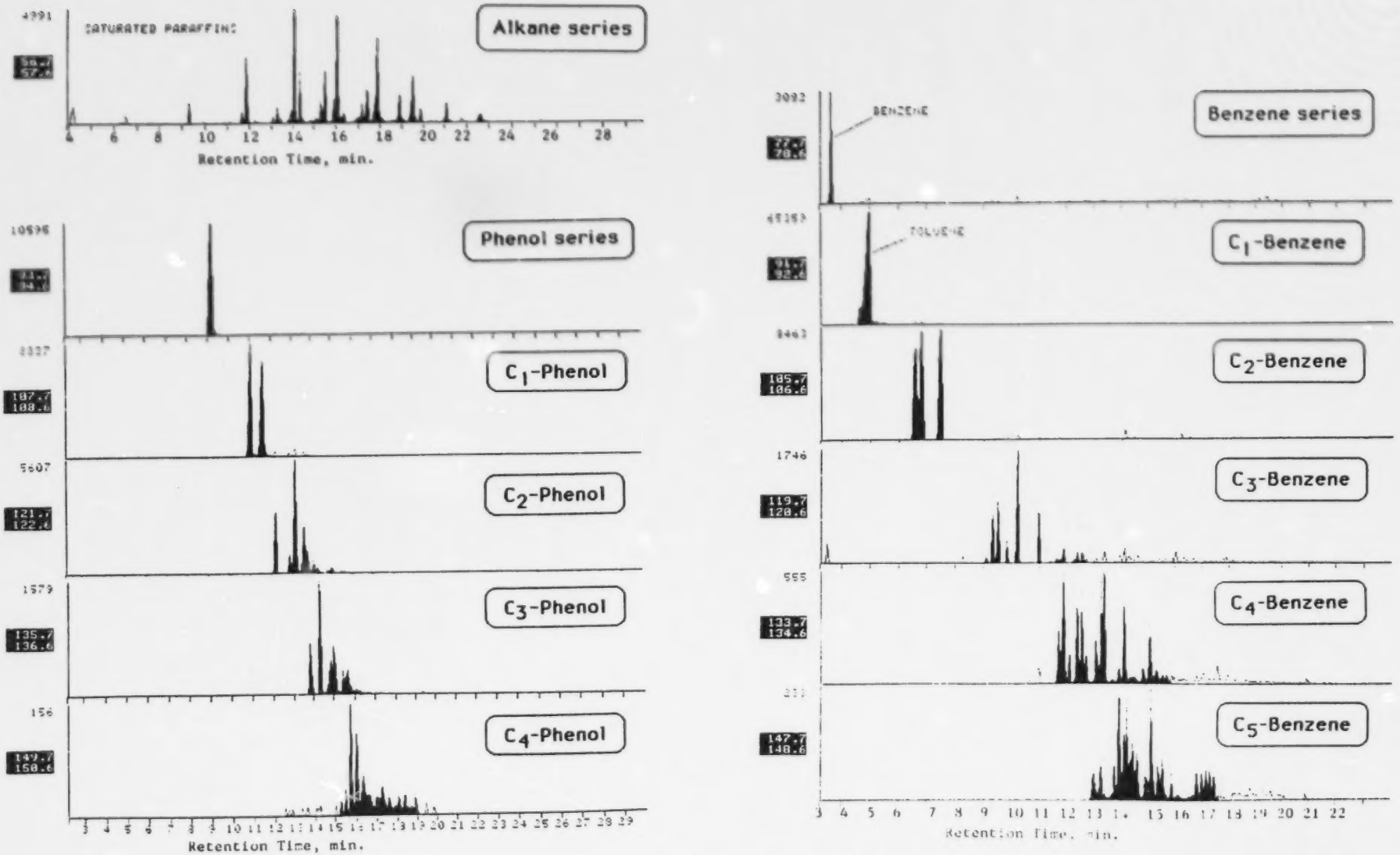
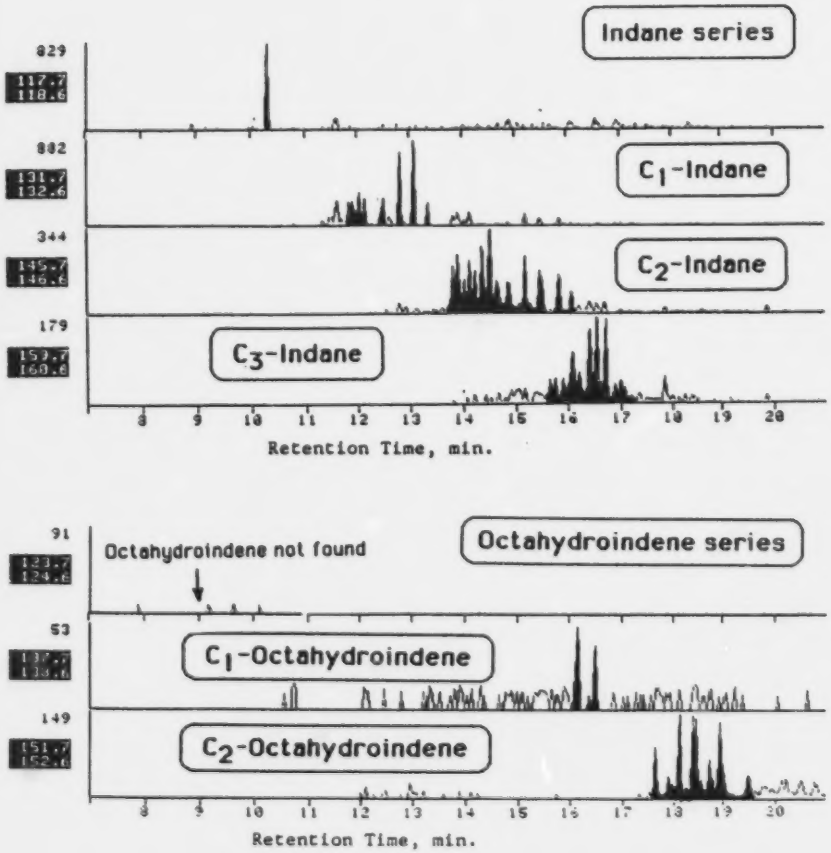
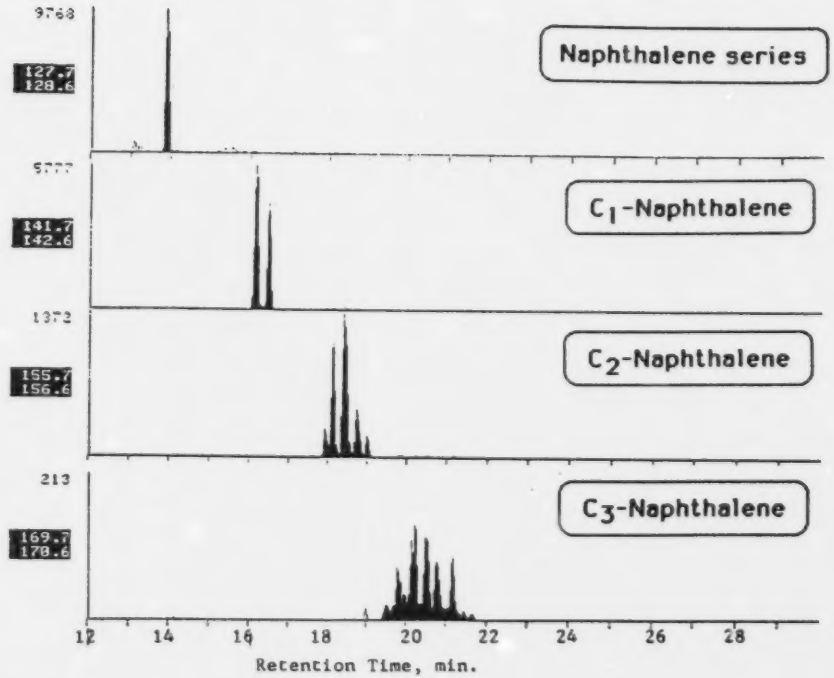


FIGURE 7B(continued)

SELECTIVE ION MONITORING OF DEVCO
COAL TAR DISTILLATE FRACTION #1





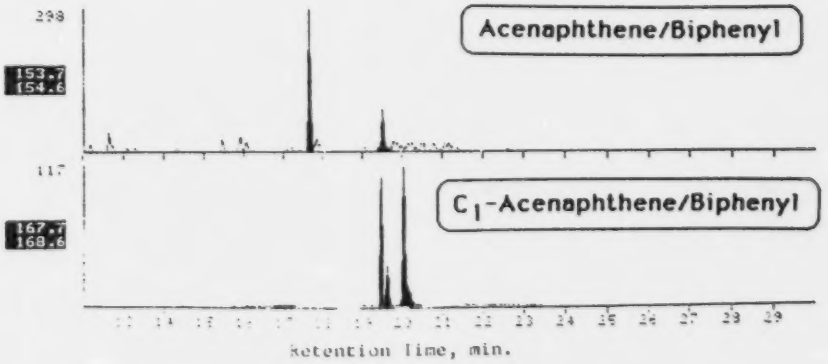
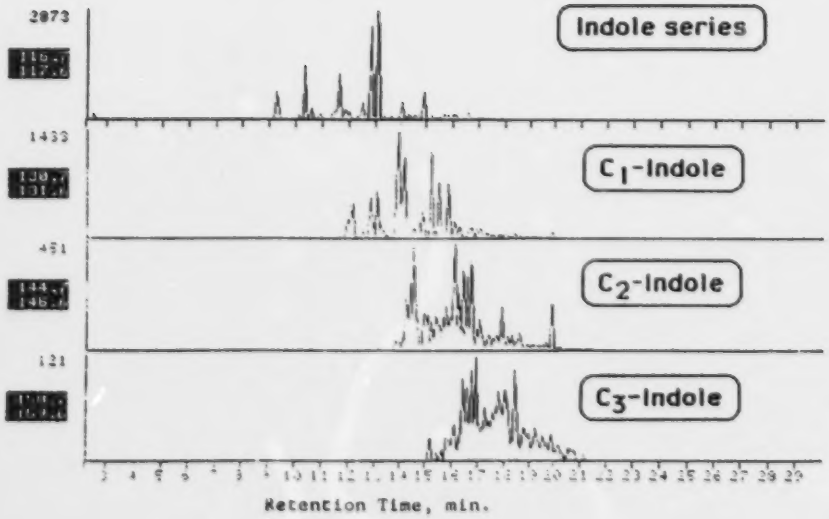
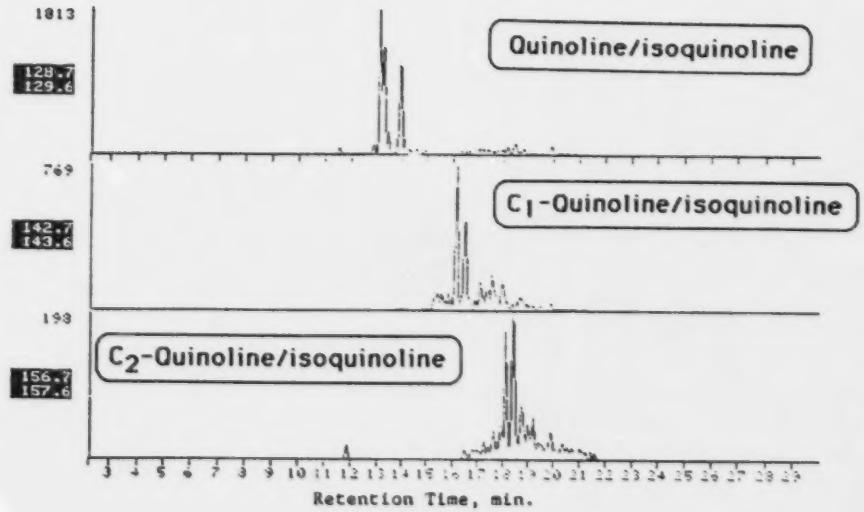


FIGURE 7B(continued)

SELECTIVE ION MONITORING OF DEVCO
COAL TAR DISTILLATE FRACTION #1





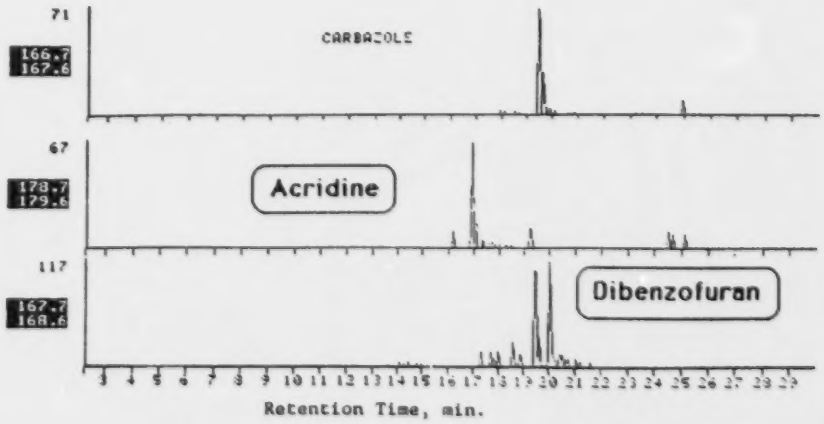


TABLE 12

COMPOUND IDENTIFIED IN DEVCO TAR DISTILLATE
FRACTION #1 (IBP - 110°C)

Peak #	Retention Time, min.(a)	Compound Identified	Weight % (b)
1	5.52	Benzene	0.179
2	8.40	Toluene	52.495
3	11.61	Ethylbenzene	3.706
4	11.88	o-Xylene	2.849
5	12.79	p-Xylene	3.521
6	13.98	1-Ethyl-2-methylbenzene	1.589
7	15.41	Phenol	1.470
8	18.21	Methylphenol	1.478
9	18.87	Methylphenol	1.737
10	19.48	1-Undecene	0.328
11	19.74	n-Undecane	0.404
12	20.38	Dimethylphenol	0.434
13	21.13	Dimethylphenol	0.269
14	21.56	Dimethylphenol	1.348
15	22.16	1-Methylindane	0.708
16	22.24	Methylindone	0.324
17	22.49	Quinoline	0.304
18	22.62	C_2-phenol	0.226
19	22.86	1-Dodecene	0.470
20	23.10	C_2-phenol	0.786
21	23.26	n-Dodecane	0.153
22	23.42	iso-Quinoline	0.153
23	23.63	Naphthalene	1.088
24	23.83	Methylindole	0.163
25	24.10	Methylindole	0.163
26	24.33	C_3-Phenol	0.181
27	24.58	C_3-Phenol	0.230
28	24.73	C_2-Naphthalene	0.274
29	24.97	C_2-Naphthalene	0.312
30	25.16	C_3-Phenol	0.185

continued....

TABLE 12
(continued)

COMPOUND IDENTIFIED IN DEVCO TAR DISTILLATE FRACTION #1 (IBP - 110°C)

Peak #	Retention time, min.(a)	Compound Identified	Weight % (b)
31	25.16	Branched C-13 alkane	0.370
32	25.43	Branched C-13 alkane	0.347
33	25.61	C_4-Phenol	0.075
34	25.75	C_4-Phenol	0.233
35	25.85	Diethylphenol	0.148
36	26.05	1-Tridecene	0.607
37	26.16	C_4-Phenol	0.092
38	26.27	n-Tridecane	0.697
39	26.43	C_4-Phenol	0.194
40	26.56	C_2-Indole	0.129
41	26.67	Methylbenzofuran	0.135
42	26.87	C_4-Phenol	0.254
43	26.96	Methylbenzofuran	0.103
44	27.22	2-Methylnaphthalene	0.750
45	27.44	C_4-Phenol	0.282
46	27.82	1-Methylnaphthalene	0.635
47	28.03	C_4-Phenol	0.262
48	28.20	Oxygen containing compound	0.174
49	28.44	3,4-Dimethylbenzaldehyde	0.145
50	28.63	Branched C-14 alkane	0.358
51	29.07	1-Tetradecene	0.358
52	29.27	n-Tetradecane	0.516
53	29.41	2-Ethylnaphthalene	0.162
54	29.70	1,8-Dimethylnaphthalene	0.223
55	30.24	C_2-Quinoline	0.195
56	30.37	C_2-Naphthalene	0.127
57	30.56	1-Ethyl-3-isopropylbenzene	0.293
58	30.83	C_2-Benzofuran	0.153
59	31.05	Branched C-15 alkane	0.525
60	31.15	Branched C-15 alkane	0.194

continued....

TABLE 12
(continued)

COMPOUND IDENTIFIED IN DEVCO TAR DISTILLATE
FRACTION #1 (IBP - 110°C)

Peak #	Retention time, min.(a)	Compound Identified	Weight % (b)
61	31.32	2,4-Dimethylquinoline	0.162
62	31.67	C_2-Naphthalene	0.288
63	31.80	C_2-Naphthalene	0.058
64	31.91	1-Pentadecene	0.211
65	32.10	n-Pentadecane	0.502
66	32.70	C_3-Naphthalene	0.212
67	32.88	C_3-Naphthalene	0.097
68	33.07	2,6-Dimethyl-4-t-butylphenol	0.307
69	33.38	Dibenzofuran	0.176
70	33.55	C_3-Naphthalene	0.117
71	34.17	C_3-Naphthalene	0.178
72	34.48	Fluorene	0.089
73	34.62	1-Hexadecene	0.165
74	34.77	n-Hexadecane	0.259
75	35.24	C_1-Acenaphthalene	0.062
76	35.48	C_4-Naphthalene	0.139
77	35.90	4-Methyl-dibenzofuran	0.151
78	36.39	Methyldimethylbenzofuran	0.153
79	36.61	Methyldimethylbenzofuran	0.096
80	36.76	C_1-Carbazole	0.123
81	37.01	C_1-Carbazole	0.100
82	37.17	1-Heptadecene	0.122
83	37.48	n-Heptadecane	0.156
84	37.86	Methylfluorene	0.054
85	38.03	Methylfluorene	0.048
86	38.15	Methylfluorene	0.115
87	38.64	C_2-carbazole	0.078
88	38.84	C_2-carbazole	0.102
89	39.28	1-Octadecene	0.091
90	39.61	n-Octadecane	0.145
91	39.74	Phenanthrene	0.115

(a) From high resolution capillary GC analysis; see Section 5.1 for details.
(b) See Table 13 for hydrocarbon/compound group type classification.

TABLE 13

SUMMARY OF HYDROCARBON AND DERIVATIVE GROUP TYPE DISTRIBUTION OF DEVCO DISTILLATE FRACTION #1 (1BP-110°C)

Hydrocarbon and Derivative Group - Type	Distribution Weight%
1. 1-Alkenes	2.35
2. n- and branched-Alkanes	5.26
3. Benzenes	64.34
4. Indenes	1.03
5. Naphthalenes	3.95
6. 3-Ring polynuclear aromatics	0.37
7. Phenols	9.91
8. Other oxygenated compounds (a)	1.29
9. Nitrogen containing compounds (b)	1.90
Total accountable (c)	90.40%

(a) Oxo-compounds, benzofuran and dibenzofuran.
(b) Including indole, quinoline and traces of carbazole and acridine.
(c) Sulphur compounds not identified.

type distribution of components found in distillate fraction #1 are presented in Table 13. It was noted that in this fraction the composition was dominated by alkylbenzenes (64%) and phenols (10%).

The HRGC and GC-MS traces of the major distillate fractions #2 are shown in Figures 8 and 9 respectively. About 130 GC peaks were observed, among which some 110 compounds were identified (Table 14). The presence of the various homologous series was confirmed by SIM as demonstrated in Figure 10. Detailed study shows that alkylbenzenes, n-alkane/1-alkene pairs (C_{12}~C_{30}), alkyl substituted naphthalenes, and phenols dominated the distillate, together with minor amounts of fluorenes, biphenyls/acenaphthenes, phenanthrenes/anthracenes and trace amounts of dibenzofurans and carbazoles. From the detailed study and SIM outputs (see Table 14) it was found that the distillate fraction #2 is composed of 41% alkylbenzenes, 7% naphthalenes, 6% phenols, 17% alkanes, 4% olefins, 2% dibenzofurans, 2% carbazoles and 5% other identified compounds. 84 wt.% of the component was identified, classified and summarized in Table 15.

It is interesting to note that the chemical structure of distillate fraction #2 is somehow simpler than that of the benzene soluble fraction (ref. 2, p. 116-118), which contains some 190 GC peaks. The major difference between the distillate fraction #2 and the benzene soluble asphaltene fraction is that fewer 4-ring aromatics and none of 5-ring aromatics are present in the distillate. Although the two samples contain essentially the same building components, yet their component distributions are very different. The distillate tends to contain more lighter components as indicated by the GC peak clusters appearing early on the retention time scale, while the benzene soluble asphaltene is dominated by larger aromatic species which appear later on the time scale. This is obviously attributable to the unavoidable partial thermal degradation of heavy components during the distillation process.

FIGURE 8 HRGC OUTPUT OF DISTILLATE FRACTION #2

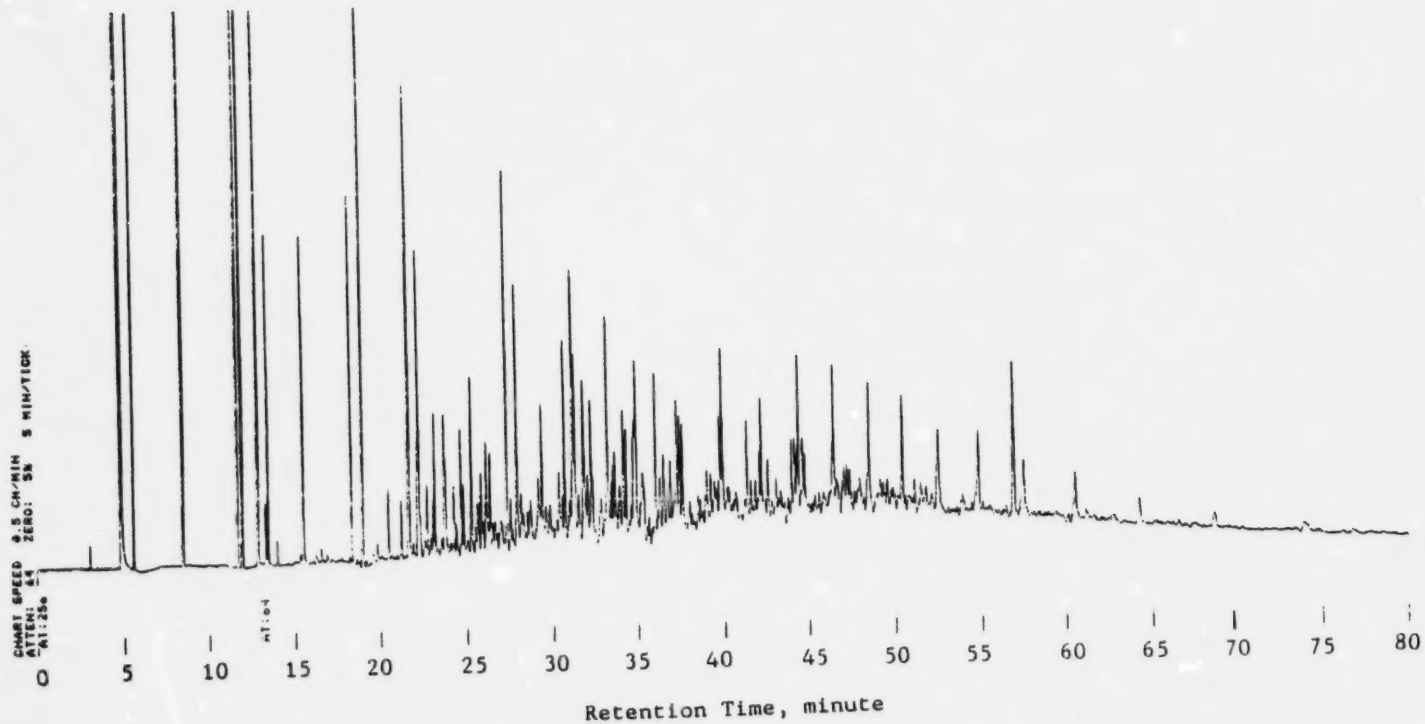


FIGURE 9 TOTAL ION OUTPUT OF DISTILLATE FRACTION #2

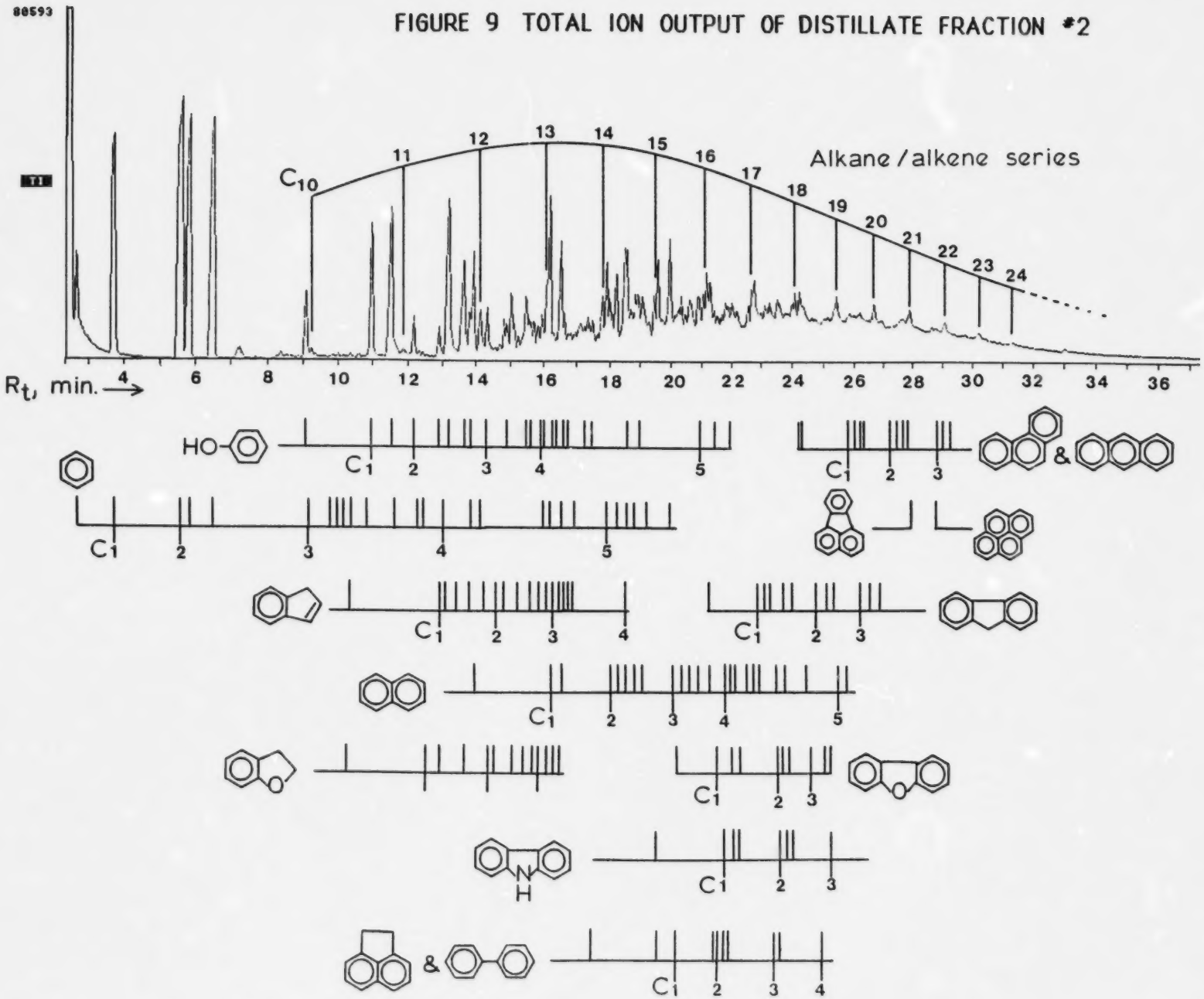


FIGURE 10

SELECTIVE ION MONITORING OF DEVCO
COAL TAR DISTILLATE FRACTION #2

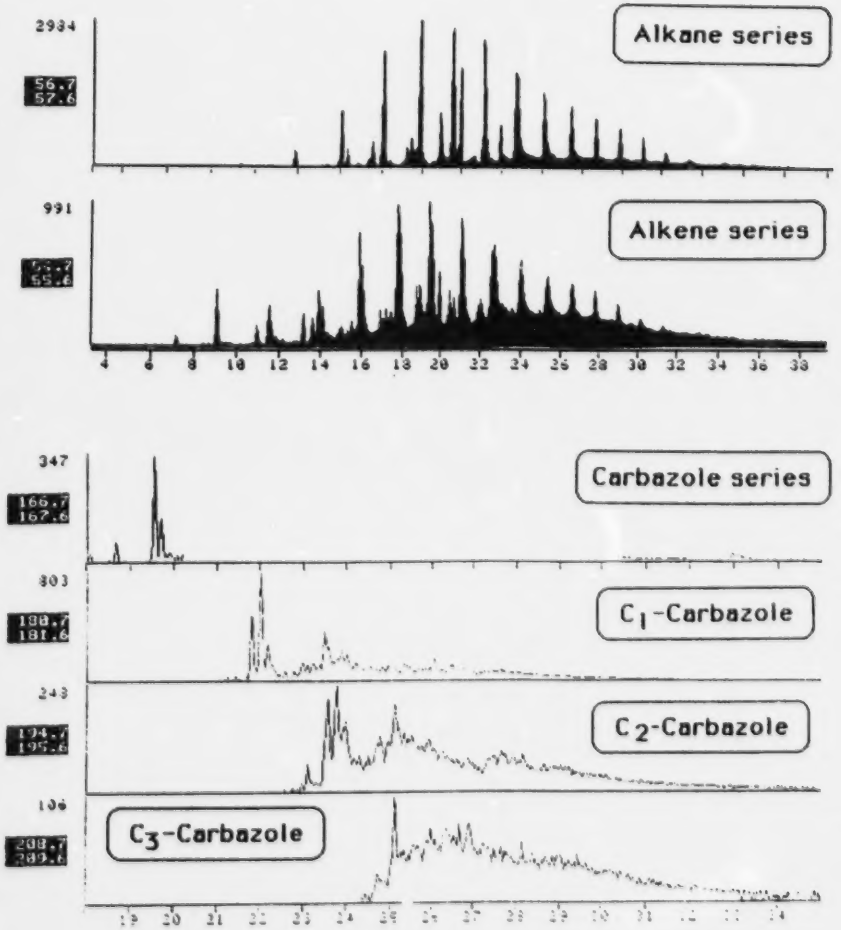


FIGURE 10

SELECTIVE ION MONITORING OF DEVCO
COAL TAR DISTILLATE FRACTION #2

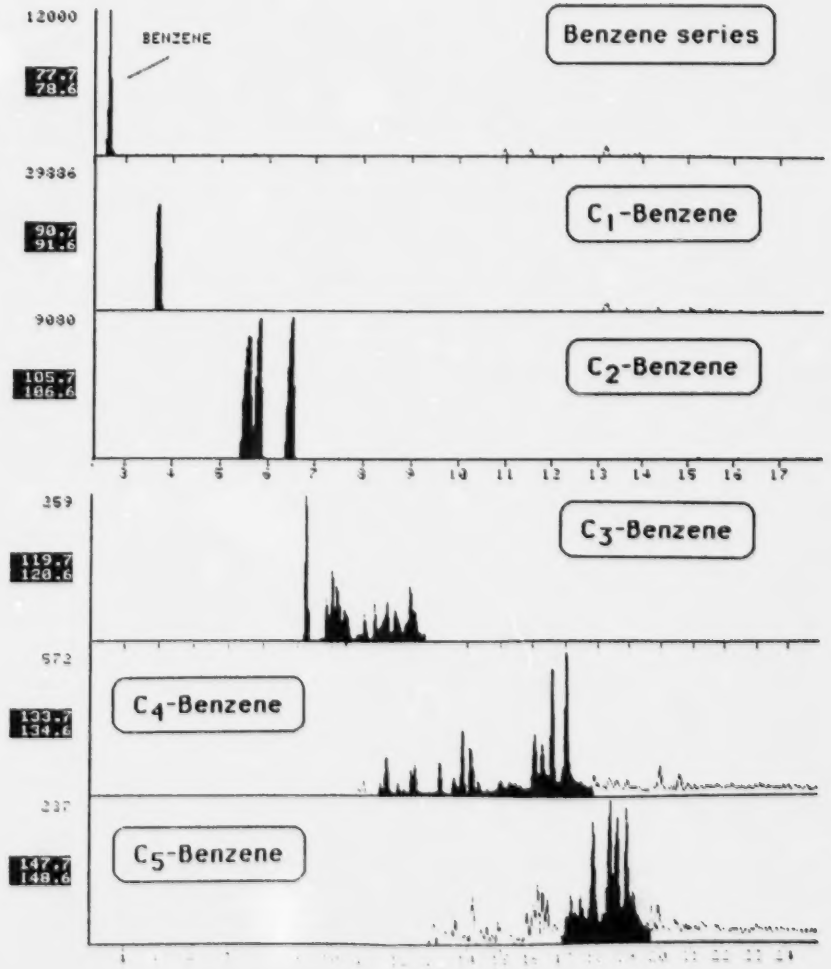


FIGURE 10 (continued)

SELECTIVE ION MONITORING OF DEVCO
COAL TAR DISTILLATE FRACTION #2

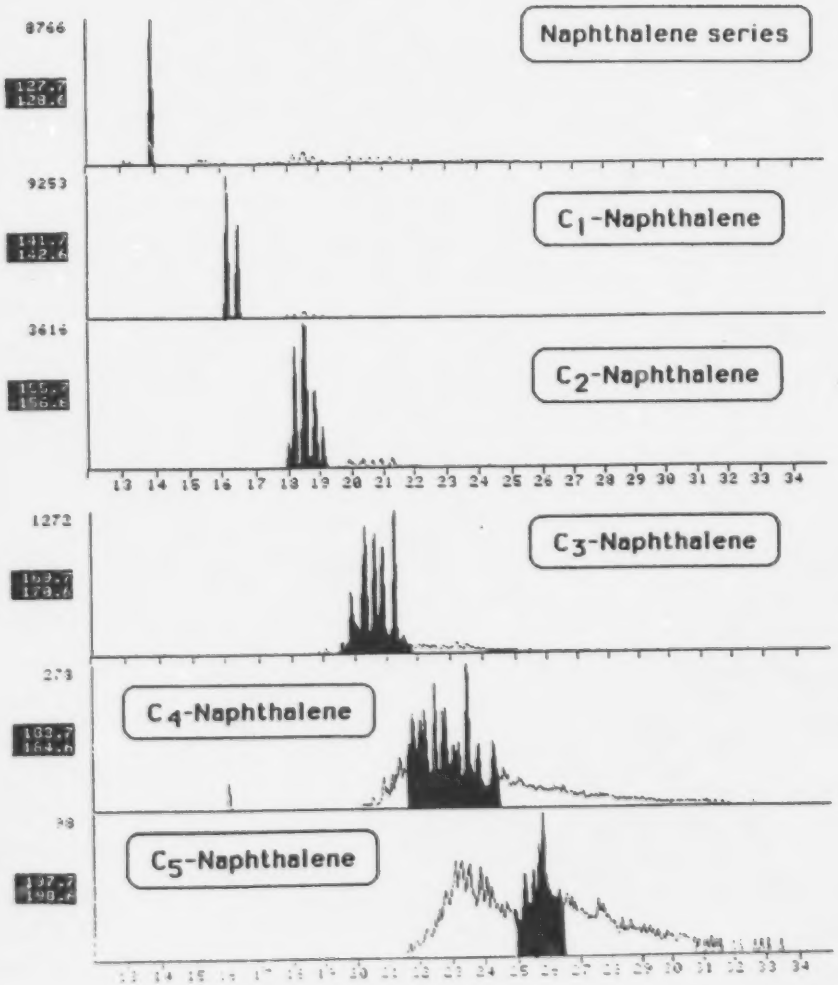


FIGURE 10 (continued)

SELECTIVE ION MONITORING OF DEVCO
COAL TAR DISTILLATE FRACTION #2

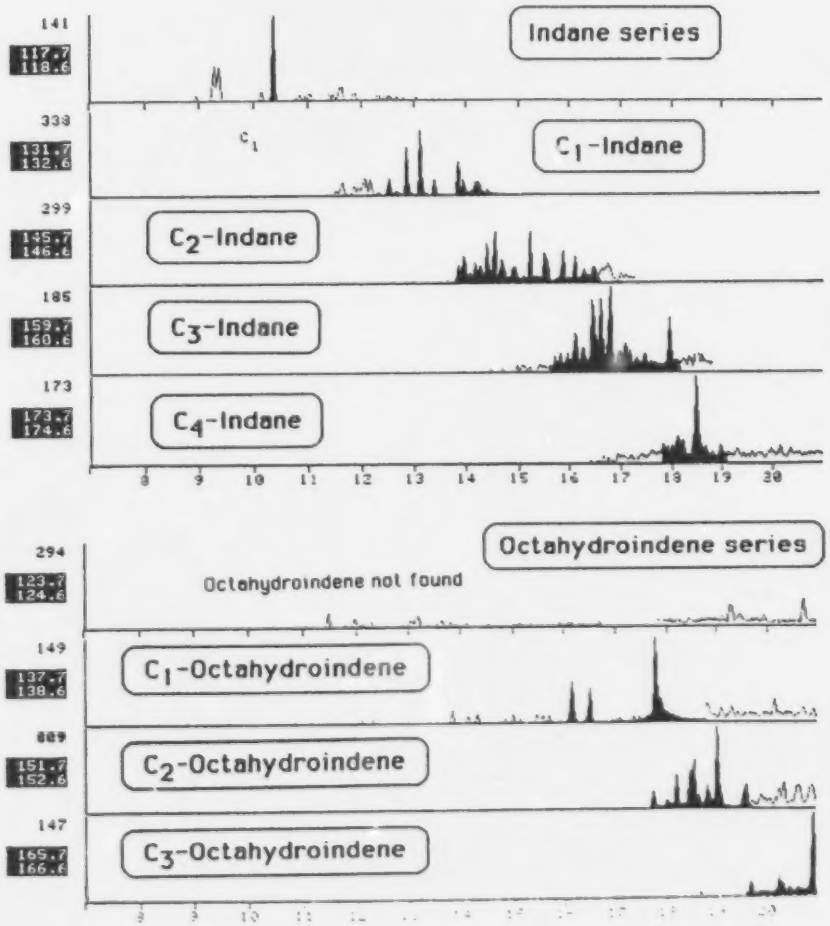


FIGURE 10 (continued)

SELECTIVE ION MONITORING OF DEVCO
COAL TAR DISTILLATE FRACTION #2

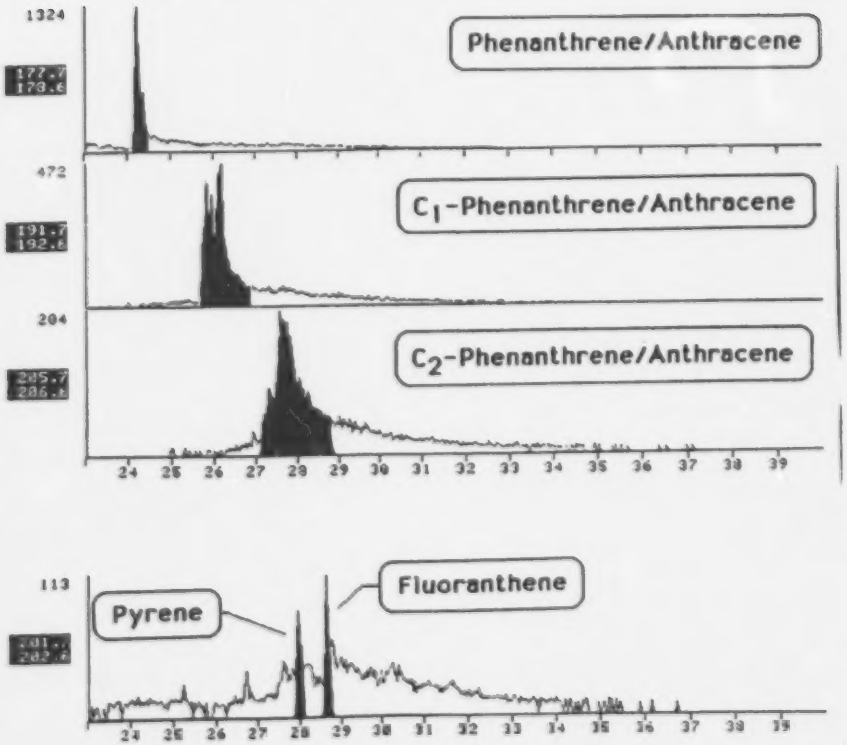


FIGURE 10 (continued)

SELECTIVE ION MONITORING OF DEVCO
COAL TAR DISTILLATE FRACTION #2

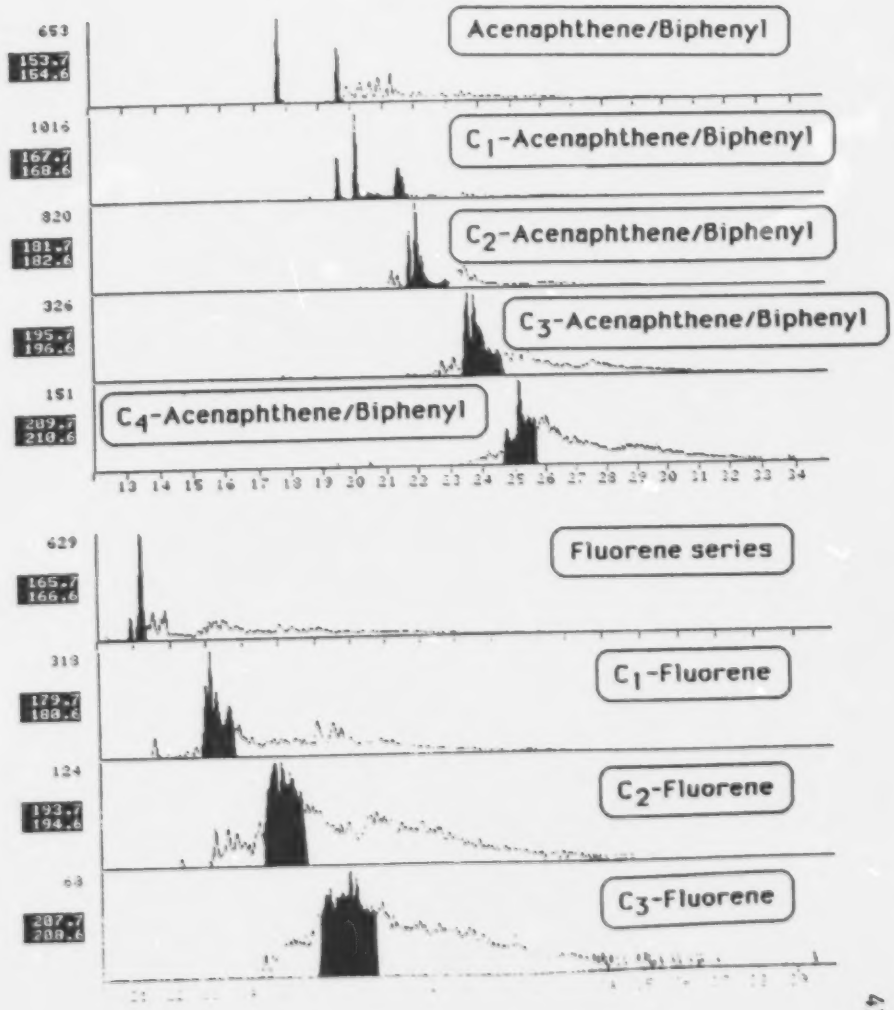


FIGURE 10 (continued)

SELECTIVE ION MONITORING OF DEVCO
COAL TAR DISTILLATE FRACTION #2

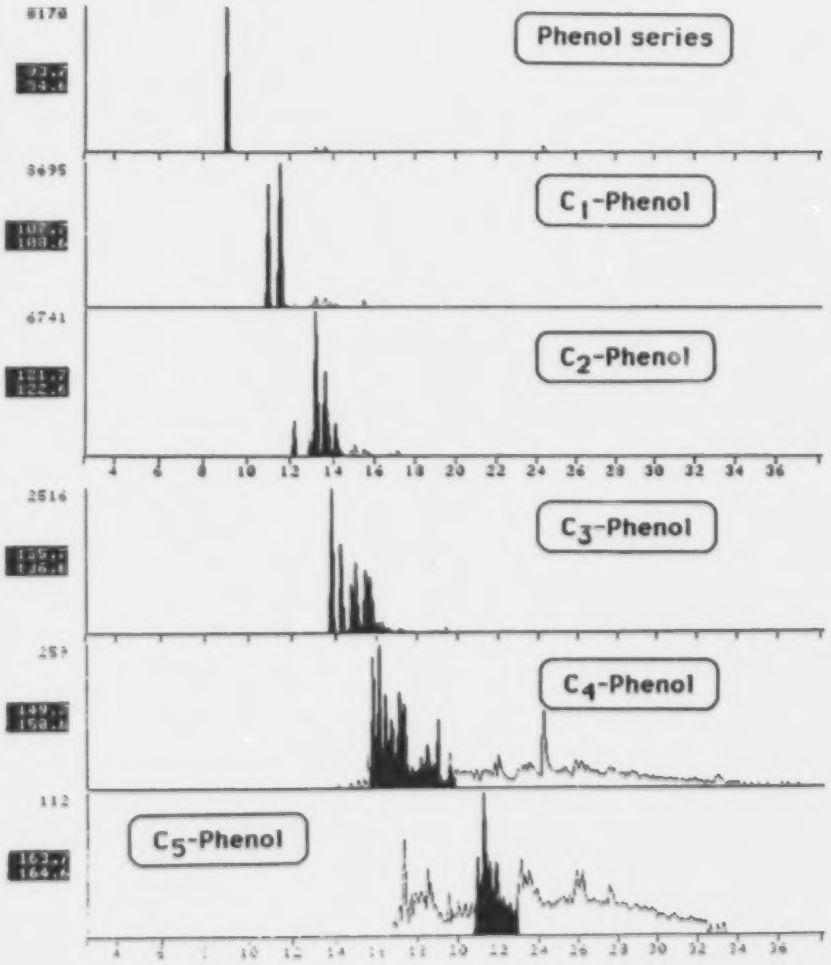


FIGURE 10 (continued)

SELECTIVE ION MONITORING OF DEVCO
COAL TAR DISTILLATE FRACTION #2

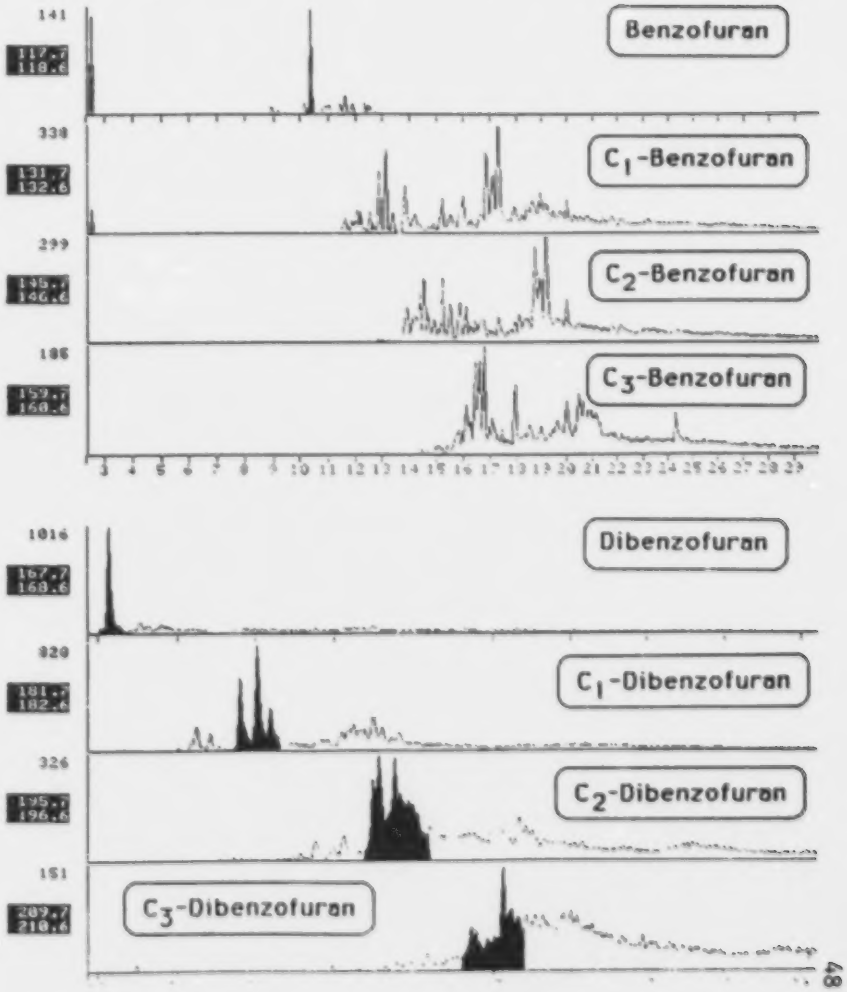


TABLE 14

COMPOUND IDENTIFIED IN DEVCO TAR DISTILLATE
FRACTION #2 (110 - 390°C)

Peak #	Retention Time, min.(a)	Compound Identified	Weight % (b)
1	5.58	Benzene	2.954
2	8.45	Toluene	12.584
3	11.70	Ethylbenzene	11.269
4	11.98	o-Xylene	6.342
5	12.88	p-Xylene	6.628
6	13.46	1-Ethyl-2-methylbenzene	0.504
7	15.49	Phenol	0.484
8	18.30	Methylphenol	0.595
9	18.97	Methylphenol	1.152
10	20.49	Dimethylphenol	0.145
11	21.24	Dimethylphenol	0.131
12	21.67	Dimethylphenol	0.990
13	22.26	1-Methylindane	0.753
14	22.74	C_2-Phenol	0.157
15	22.96	1-Dodecene	0.085
16	23.07	C_2-Phenol	0.091
17	23.19	n-Dodecane	0.297
18	23.75	Naphthalene	0.473
19	24.29	C_3-Phenol	0.180
20	24.44	C_3-Phenol	0.116
21	24.69	C_2-Naphthalene	0.243
22	24.83	C_2-Naphthalene	0.164
23	25.29	C_3-Phenol	0.377
24	25.63	C_3-Phenol	0.121
25	25.73	C_3-Phenol	0.114
26	25.86	Diethylphenol	0.182
27	25.98	C_3-Phenol	0.097
28	26.16	1-Tridecene	0.379
29	26.38	n-Tridecane	0.234
30	26.54	C_4-Phenol	0.115
31	26.68	C_4-Phenol	0.140
32	26.78	Methylbenzofuran	0.061
33	27.00	Methylbenzofuran	0.203
34	27.35	2-Methylnaphthalene	0.711
35	27.57	C_4-Phenol	0.194
36	27.68	Methylbenzofuran	0.087
37	27.77	Methylbenzofuran	0.050
38	27.95	1-Methylnaphthalene	0.668
39	28.18	C_4-Phenol	0.232
40	28.30	Oxygen containing compound	0.148
41	28.44	4-Methoxylphenol	0.071
42	28.55	3,4-Dimethylbenzaldehyde	0.126
43	28.72	Branched C-14 alkane	0.364
44	29.18	1-Tetradecene	0.451
45	29.38	n-Tetradecane	0.400
46	29.63	2-Ethylnaphthalene	0.198
47	29.85	1,8-Dimethylnaphthalene	0.238
48	30.37	C_2-Naphthalene	0.271
49	30.55	C_2-Naphthalene	0.193
50	30.69	1-Ethyl-3-isopropylbenzene	0.485
51	31.00	C_2-Benzofuran	0.292
52	31.18	C_2-Naphthalene	0.757
53	31.29	C_2-Naphthalene	0.415
54	31.51	2,4-Dimethylquinoline	0.322
55	31.80	C_2-Naphthalene	0.577

continued...

TABLE 14
(continued)

COMPOUND IDENTIFIED IN DEVCO TAR DISTILLATE
FRACTION #2 (110 - 390°C)

Peak #	Retention Time, min.(a)	Compound Identified	Weight % (b)
56	31.94	C_2-Naphthalene	0.131
57	32.04	1-Pentadecene	0.245
58	32.23	n-Pentadecane	0.588
59	32.84	C_3-Naphthalene	0.383
60	33.04	C_3-Naphthalene	0.125
61	33.21	2,6-Dimethyl-4-t-butylphenol	0.701
62	33.51	Dibenzofuran	0.202
63	33.64	C_3-Naphthalene	0.350
64	34.30	C_3-Naphthalene	0.338
65	34.51	C_3-Naphthalene	0.123
66	34.62	Fluorene	0.174
67	34.78	1-Hexadecene	0.424
68	34.90	n-Hexadecane	0.627
69	35.37	Methlacenaphthene	0.163
70	35.54	2-Mehyl-1-naphthol	0.130
71	35.66	C_4-Naphthalene	0.179
72	35.84	4-Methyldibenzofuran	0.570
73	36.30	Branched C-17 alkane	0.372
74	36.52	Methyldibenzofuran	0.452
75	36.77	Methyldibenzofuran	0.344
76	36.92	Methylcarbazole	0.282
77	37.15	Methylcarbazole	0.173
78	37.31	1-Heptadecene	0.478
79	37.63	n-Heptadecane	0.564
80	38.05	Methylfluorene	0.301
81	38.17	Methylfluorene	0.136
82	38.27	Methylfluorene	0.094
83	38.79	C_2-Carbazole	0.210
84	39.03	C_2-Carbazole	0.518
85	39.47	1-Octadecene	0.363
86	39.57	n-Octadecane	0.239
87	39.76	Phenanthrene	0.384
88	40.17	Anthracene	0.319
89	42.82	C_1-Phenanthrene/anthracene	0.293
90	43.08	C_1-Phenanthrene/anthracene	0.396
91	43.49	C_1-Phenanthrene/anthracene	0.079
92	43.79	C_1-Phenanthrene/anthracene	0.355
93	43.98	1-Eicosene	0.376
94	44.15	n-Eicosane	0.450
95	46.22	1-Heneicosene	0.292
96	46.48	n-Heneicosane	0.940
97	46.64	Pyrene	0.616
98	47.52	Fluoranthene	0.250
99	48.20	1-Docosene	0.301
100	48.50	n-Docosane	1.130
101	50.45	n-Tricosane	0.843
102	52.51	n-Tetracosane	1.702
103	54.83	n-Pentacosane	1.370
104	56.87	Branched C-26 alkane	1.788
105	57.48	n-Hexacosane	1.292
106	60.58	n-Heptacosane	1.353
107	64.28	n-Octacosane	0.980
108	68.68	n-Nonacosane	0.984
109	73.99	n-C-30 alkane	1.147

(a) From high resolution capillary GC: see Section 5.1 for details.
(b) See Table 15 for hydrocarbon/compound group type classification.

TABLE 15

SUMMARY OF HYDROCARBON AND DERIVATIVE GROUP TYPE DISTRIBUTION OF DEVCO DISTILLATE FRACTION #2 (110-390°C)

Hydrocarbon and Derivative Group - Type	Distribution Weight%
1. n- and branched Alkanes	17.44
2. 1-Alkenes	3.63
3. Benzenes	40.77
4. Naphthalenes	6.52
5. Other aromatic hydrocarbons	4.45
6. Phenols	6.28
7. Benzofurans and dibenzofurans	2.26
8. Other oxygen containing compounds (a)	0.27
9. Nitrogen containing compounds (b)	1.50
10. Sulphur containing compounds (c)	1.75
Total accountable	84.97%

(a) Including oxo-compounds and benzaldehyde.
(b) Including quinolines and carbazoles.
(c) Estimated from S-content of 0.32%, with average mol. wt. 160 and 20% S content.

5.3 Detailed characterization of the nine hydrotreated liquids: series number F86, sample label 06B to 06J

The same HRGC and GC-MS experimental conditions and methodology as for the tar distillates were applied to the nine hydrotreated liquids obtained. Sample labels 06B to 06J are simplified and referred as B to J respectively throughout the text and some of the tables.

Detailed HRGC traces were collected in Figures 11 to 19 and the total ion outputs (TI) in Figures 20 to 27. All the hydrotreated liquids are shown to have similar compositional structure as reflected from the HRGC and TI traces. A summary of the detailed hydrocarbon and related compound classes found in the hydrotreated samples are collected in Table 16. GC-MS analysis at the SIM mode was also performed for most of the hydrotreated liquids (sample 06B to 06H and 06J). Figure 28 illustrates the SIM traces for the hydrotreated liquid 06B for hydrocarbon group type and oxygen containing homologs, such as phenol. All the other SIM traces (not shown) were indicated to have the same SIM outputs. This finding strongly indicates that all the hydrotreated liquids have the same or similar composition homologs, but with different degree of distribution depending on hydrotreating conditions.

Hydrogenated quinolines/isoquinolines and trace of hydrogenated acridines were found as the major nitrogen containing homologs in all the hydrotreated liquid samples. These nitrogen containing homologs are summarized in Table 17. SIM traces of these nitrogen containing homologs present in sample 06B were illustrated in Figure 29. Table 18 summarises the overall results in terms of hydrocarbon group type and derivative compound type distributions for all the detailed chemical characterizations of hydrotreated samples. All these liquids contain alkylbenzenes, alkylcyclohexanes and the alkanes, they have a total contribution in the

range of 62-71%. Naphthalenes and the two hydrogenated homologs, tetrahydronaphthalenes (i.e. tetralin) and decahydronaphthalenes (i.e. decalin) have a combined contribution in a narrow range of 8-9%. Indans and their hydrogenated forms, octahydroindene, and cyclopentanes were also found in small but variable amounts.

Phenols being the most important single heteroatomic homolog fall within the range of 2.5-4.5%. The other oxygen containing compounds were identified as the benzofurans, dibenzofurans and bicyclic ketones. The nitrogen containing compounds are dominated in the hydrogenated form of quinolines/isoquinolines and traces for the hydrogenated acridine as mentioned in the above SIM study. Chemical characterization of these hydrogenated forms of N-heterocycles and their belonging homologs, and even higher homologs (i.e. with higher ring number) has not been studied in the previous phase of work. The occurance of these hydrogenated N-containing homologs in hydrotreated coal derived liquids have also been speculated by several research groups (4,5) using GC-MS method together with postulated mechanism of formation.

The total accountable components present in the hydrotreated liquids fall within the range of 91-95 wt%. One should regard the presented results in Table 18 as semiquantitative.

5.4 Comments on sulphur species

As described above the virgin and all hydrotreated samples have been subjected to a detailed GC-MS study. Extensive searches were conducted for sulphur containing homologs such as alkyl substituted benzothiophenes, dibenzothiophenes and thiols. In all cases these sulphur homologs were not found. From the elemental analysis, the origin tar contains about 0.32% S. Assuming an average of one sulphur atom per molecule of sulphur homolog of

FIGURE 11 HRGC OUTPUT OF HYDROTREATED SAMPLE B

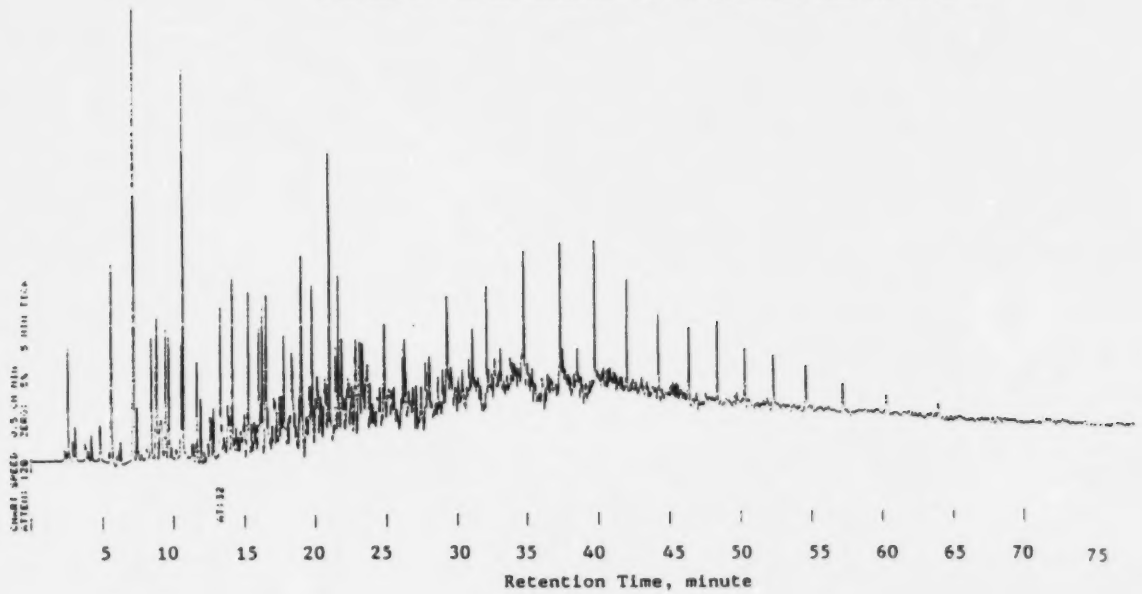


FIGURE 12 HRGC OUTPUT OF HYDROTREATED SAMPLE C

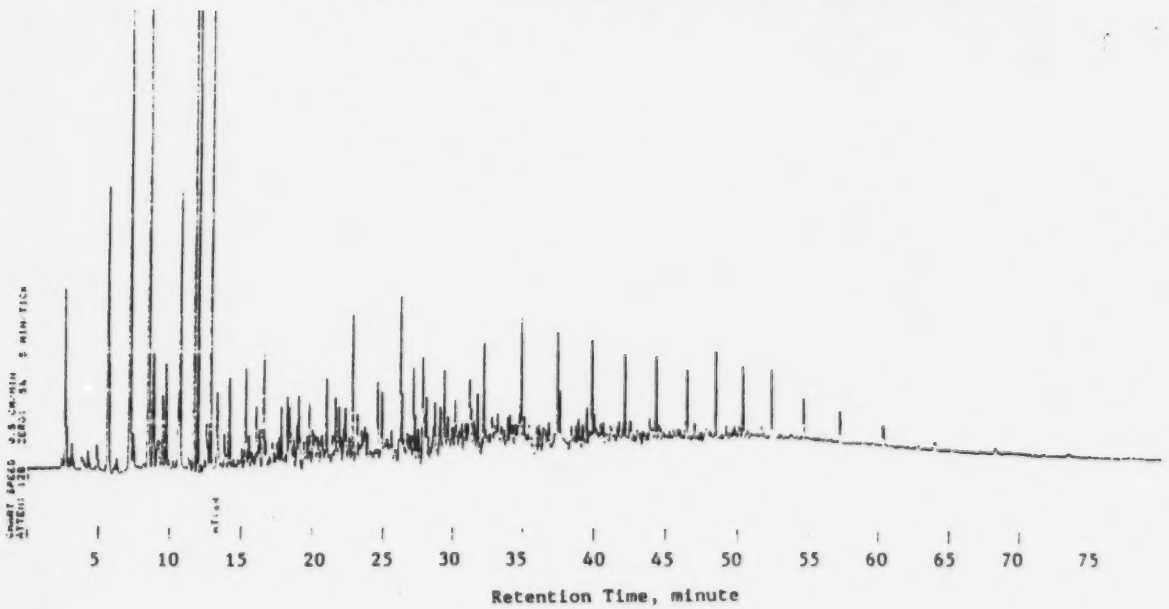


FIGURE 13 HRGC OUTPUT OF HYDROTREATED SAMPLE D

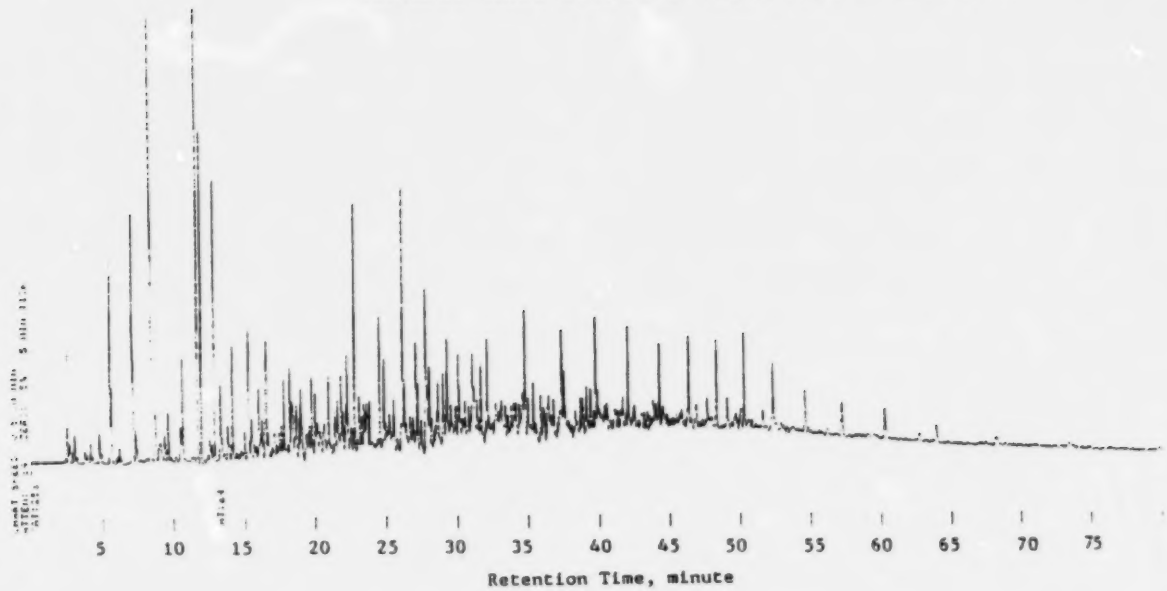


FIGURE 14 HRGC OUTPUT OF HYDROTREATED SAMPLE E

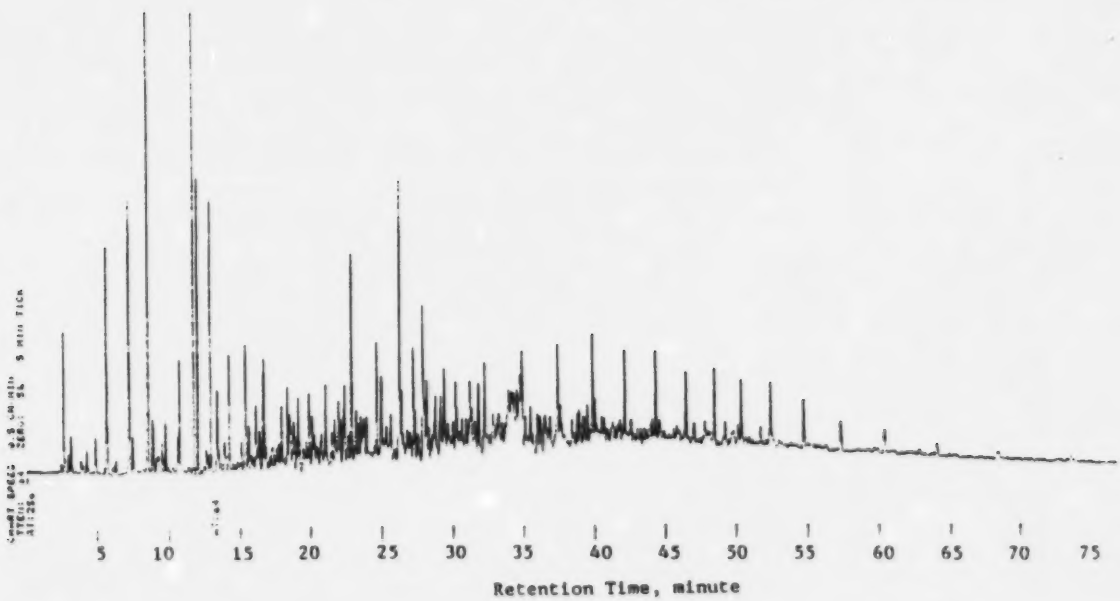


FIGURE 15 HRGC OUTPUT OF HYDROTREATED SAMPLE F

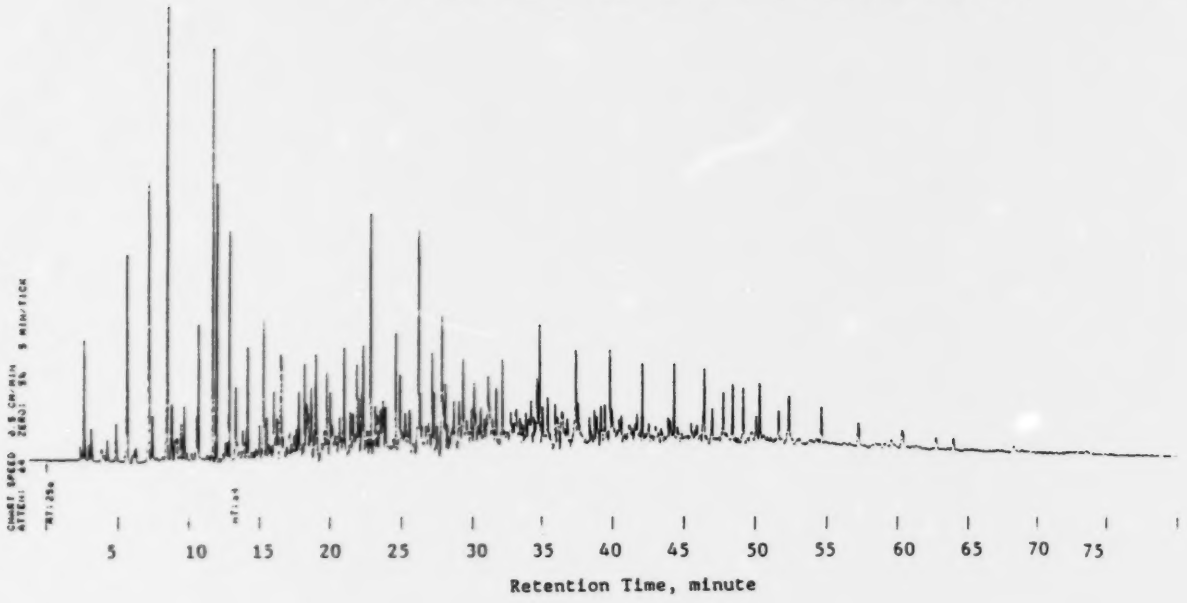


FIGURE 16 HRGC OUTPUT OF HYDROTREATED SAMPLE G

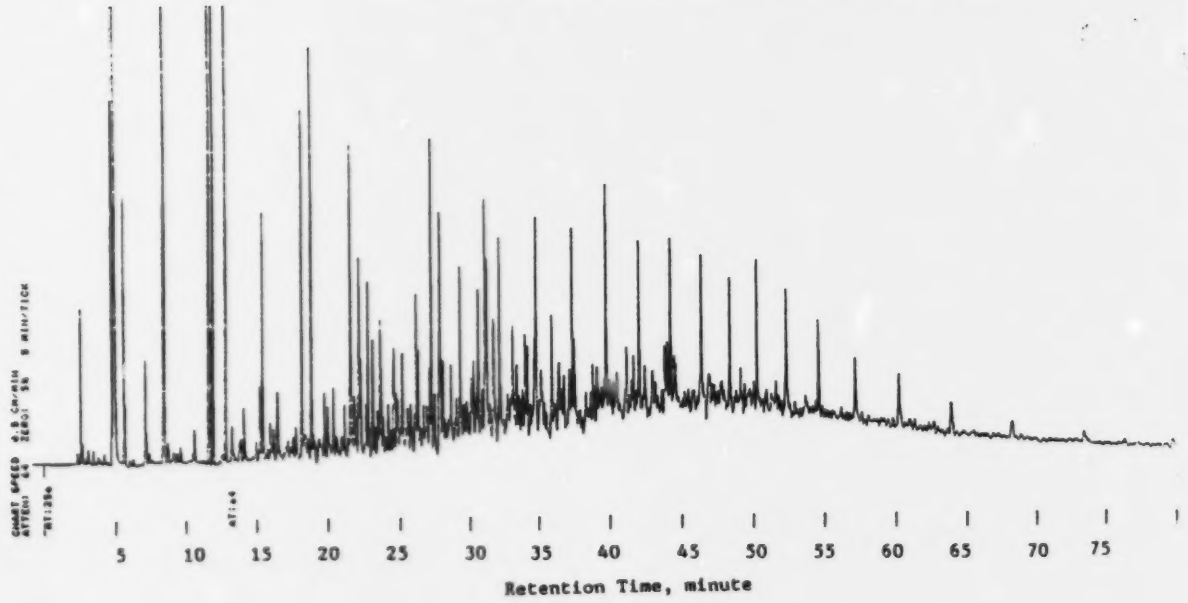


FIGURE 17 HRGC OUTPUT OF HYDROTREATED SAMPLE H

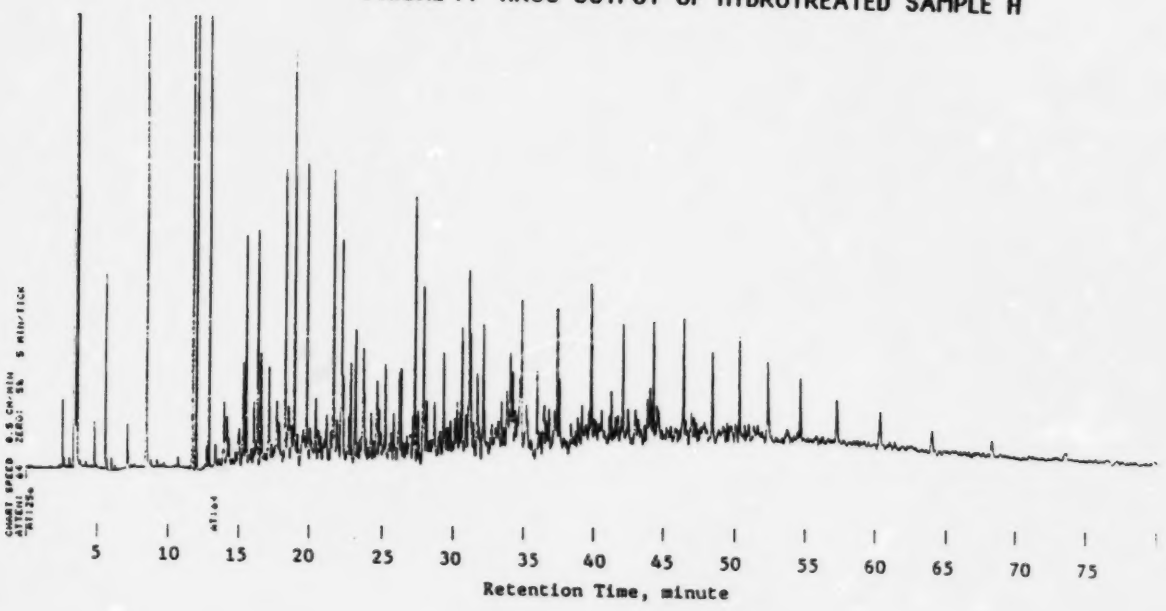


FIGURE 18 HRGC OUTPUT OF HYDROTREATED SAMPLE I

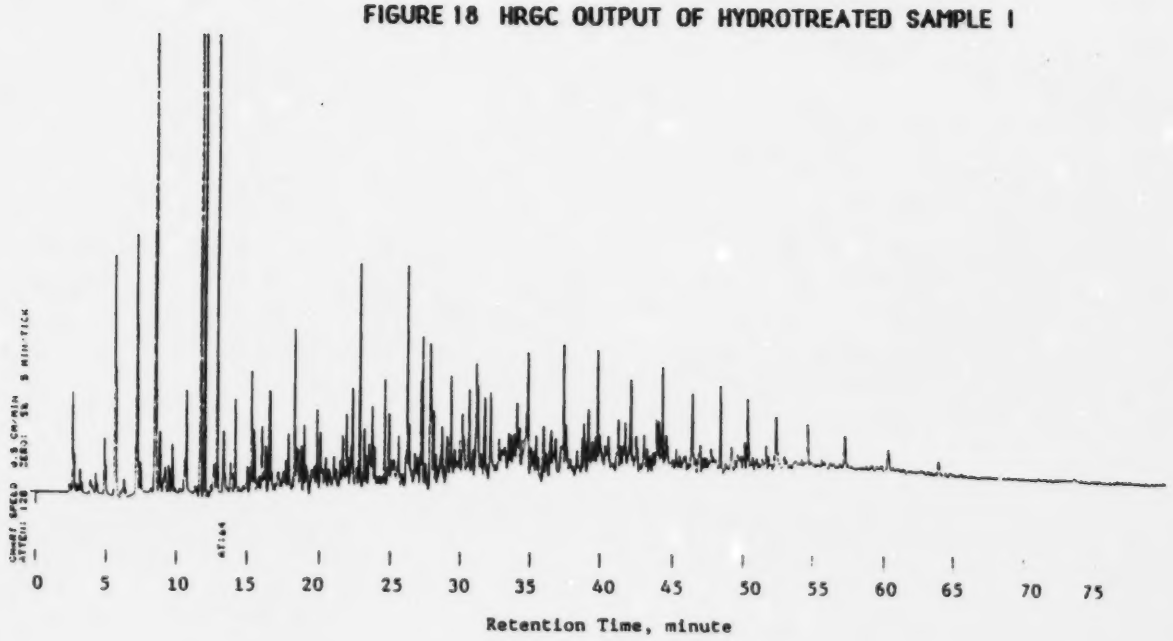


FIGURE 19 HRGC OUTPUT OF HYDROTREATED SAMPLE J

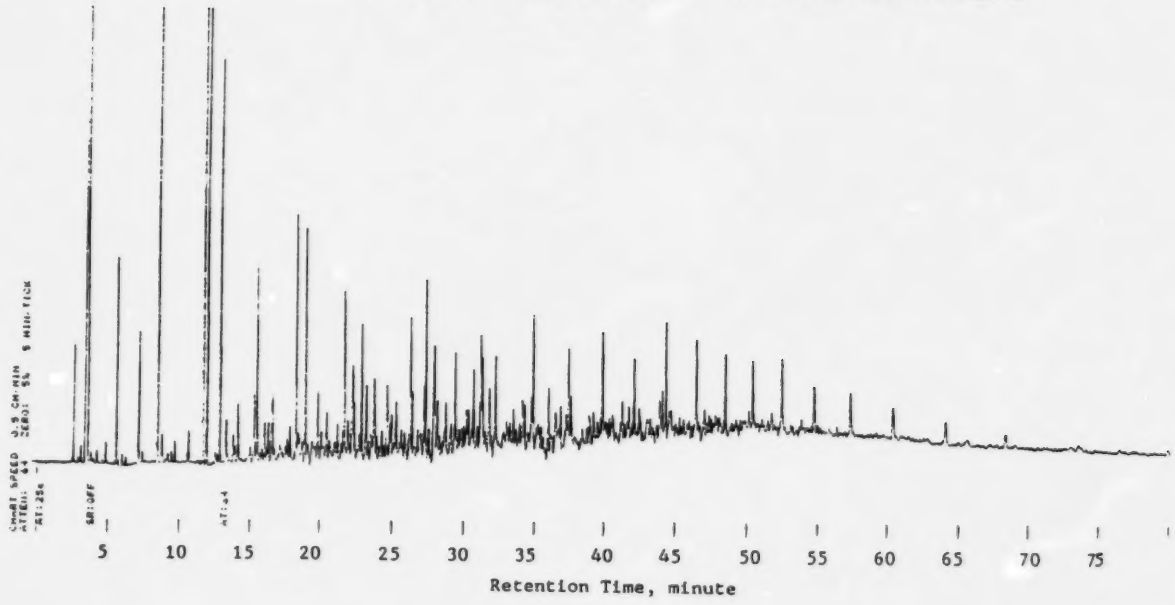


FIGURE 20 TOTAL ION OUTPUT OF HYDROTREATED SAMPLE 06B

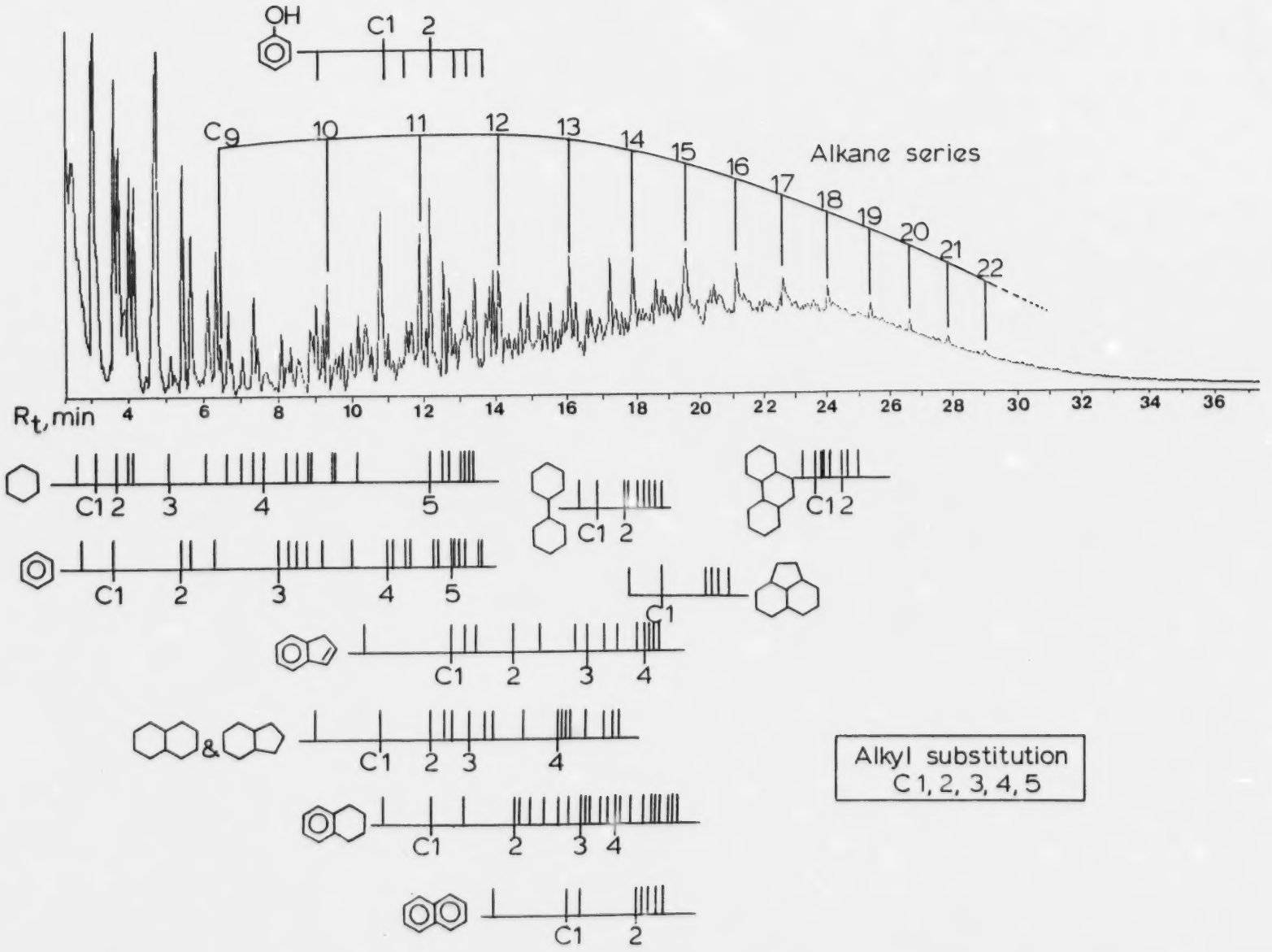


FIGURE 21 TOTAL ION OUTPUT OF HYDROTREATED SAMPLE 06C

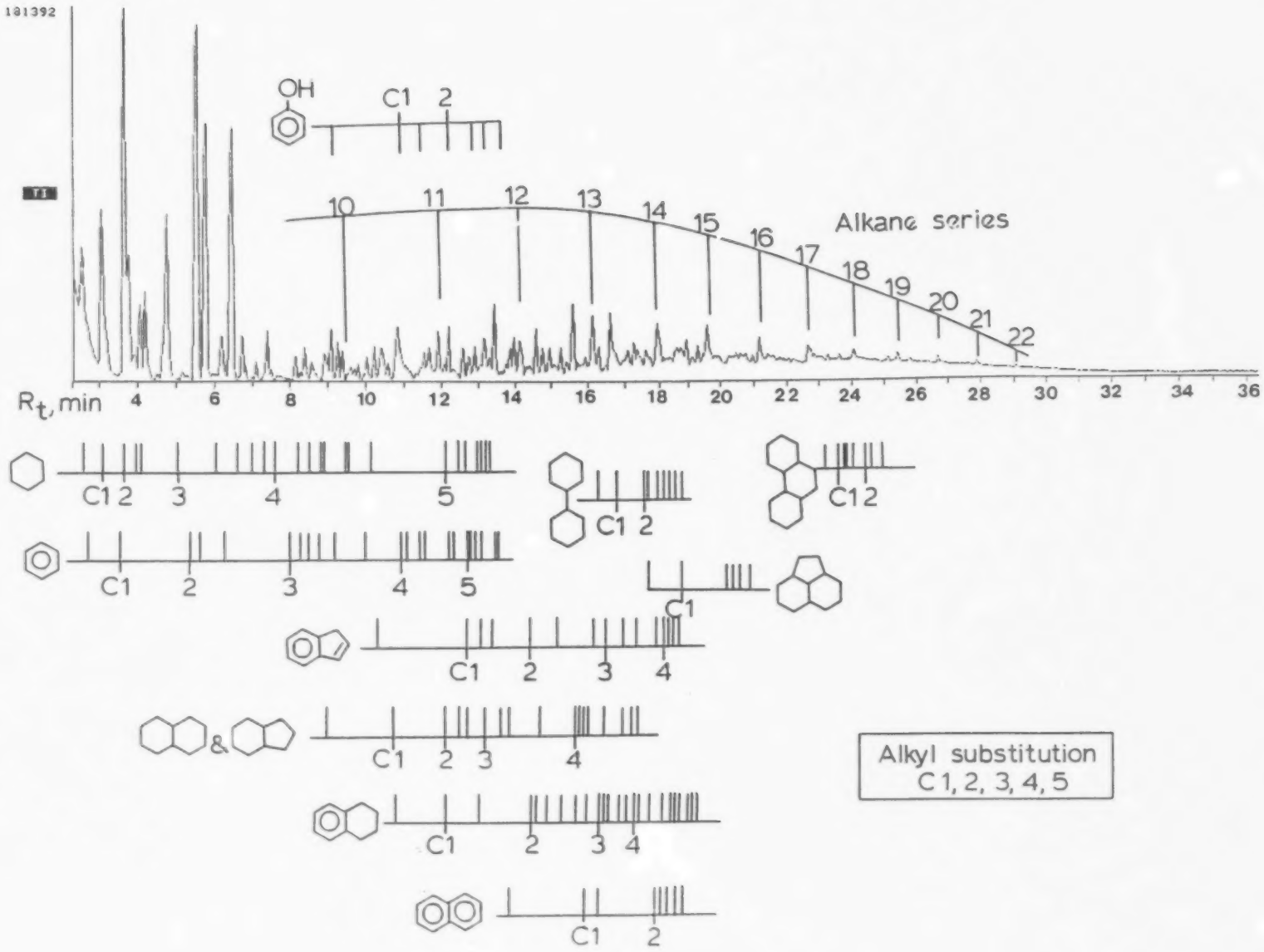


FIGURE 22 TOTAL ION OUTPUT OF HYDROTREATED SAMPLE 06D

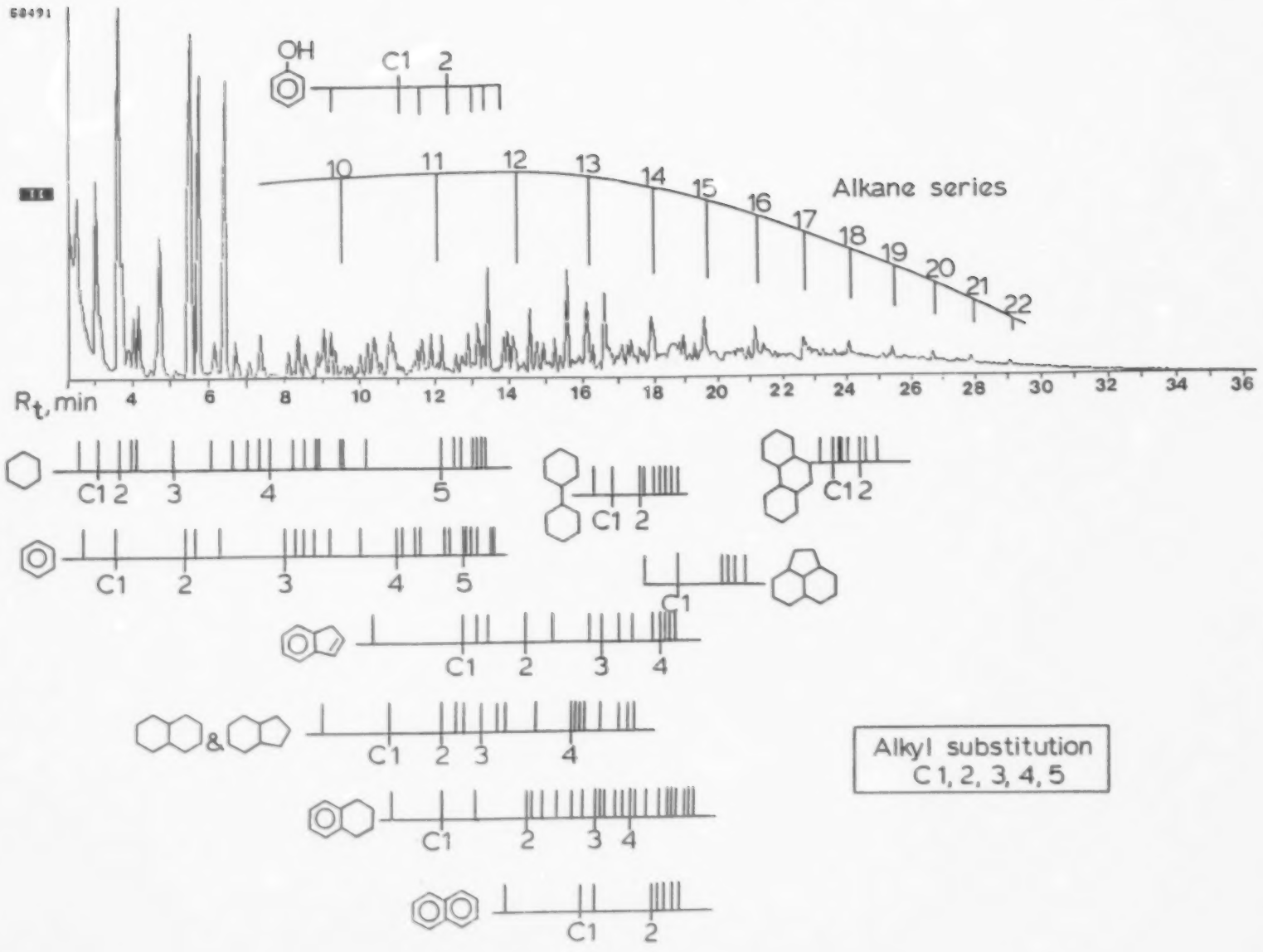


FIGURE 23 TOTAL ION OUTPUT OF HYDROTREATED SAMPLE 06E

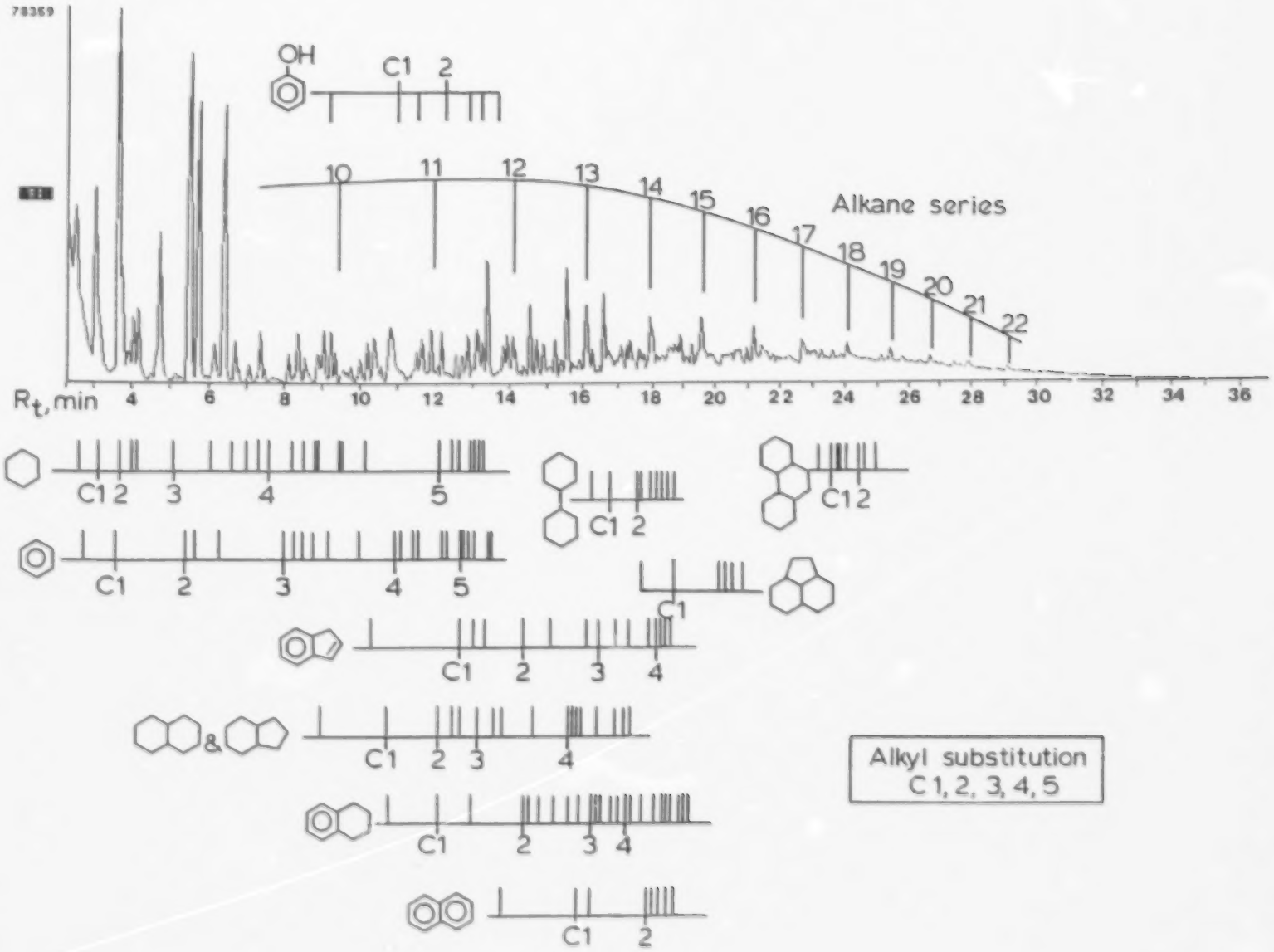


FIGURE 24 TOTAL ION OUTPUT OF HYDROTREATED SAMPLE 06F

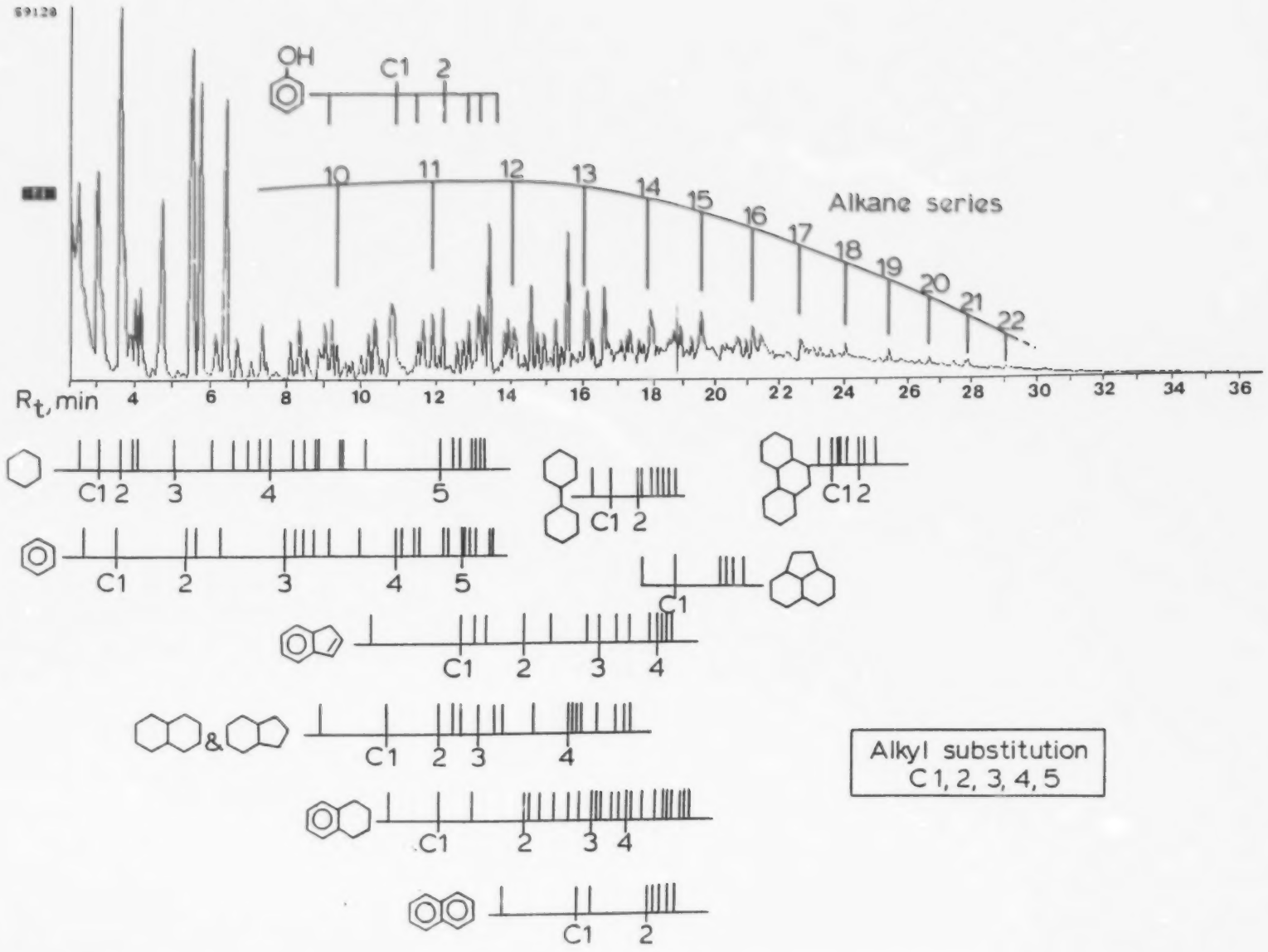


FIGURE 25 TOTAL ION OUTPUT OF HYDROTREATED SAMPLE 066

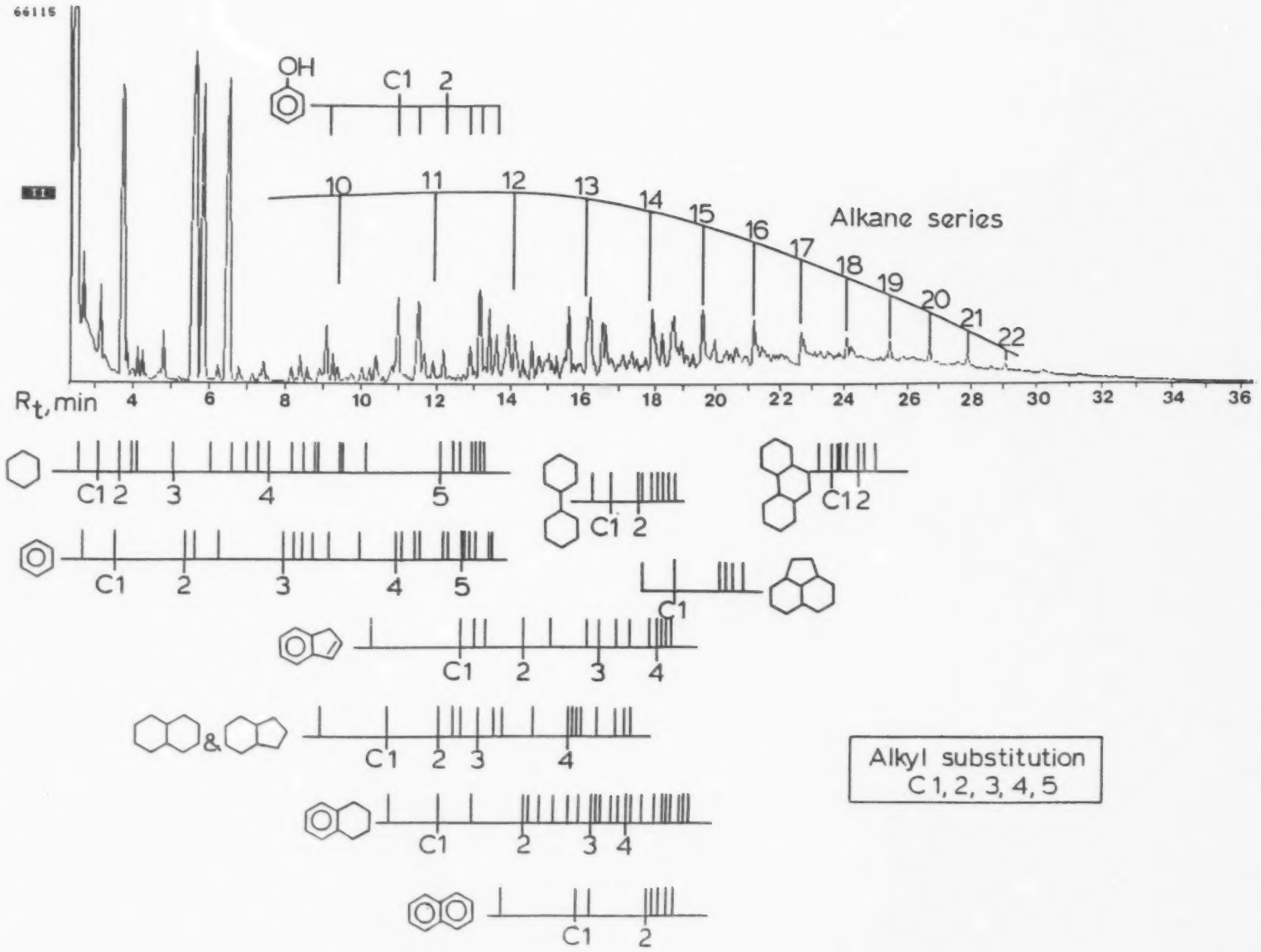


FIGURE 26 TOTAL ION OUTPUT OF HYDROTREATED SAMPLE 06H

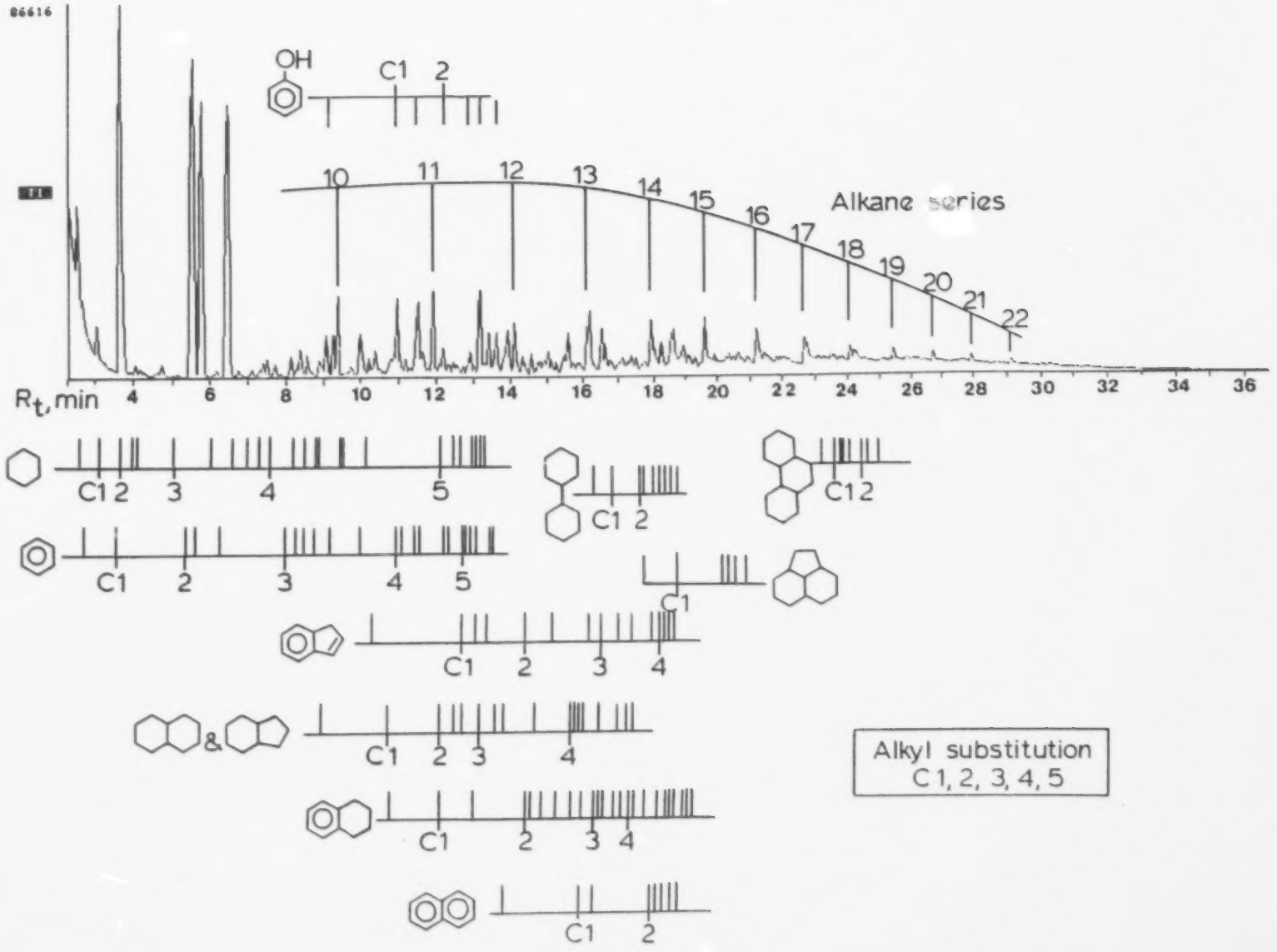


FIGURE 27 TOTAL ION OUTPUT OF HYDROTREATED SAMPLE 06J

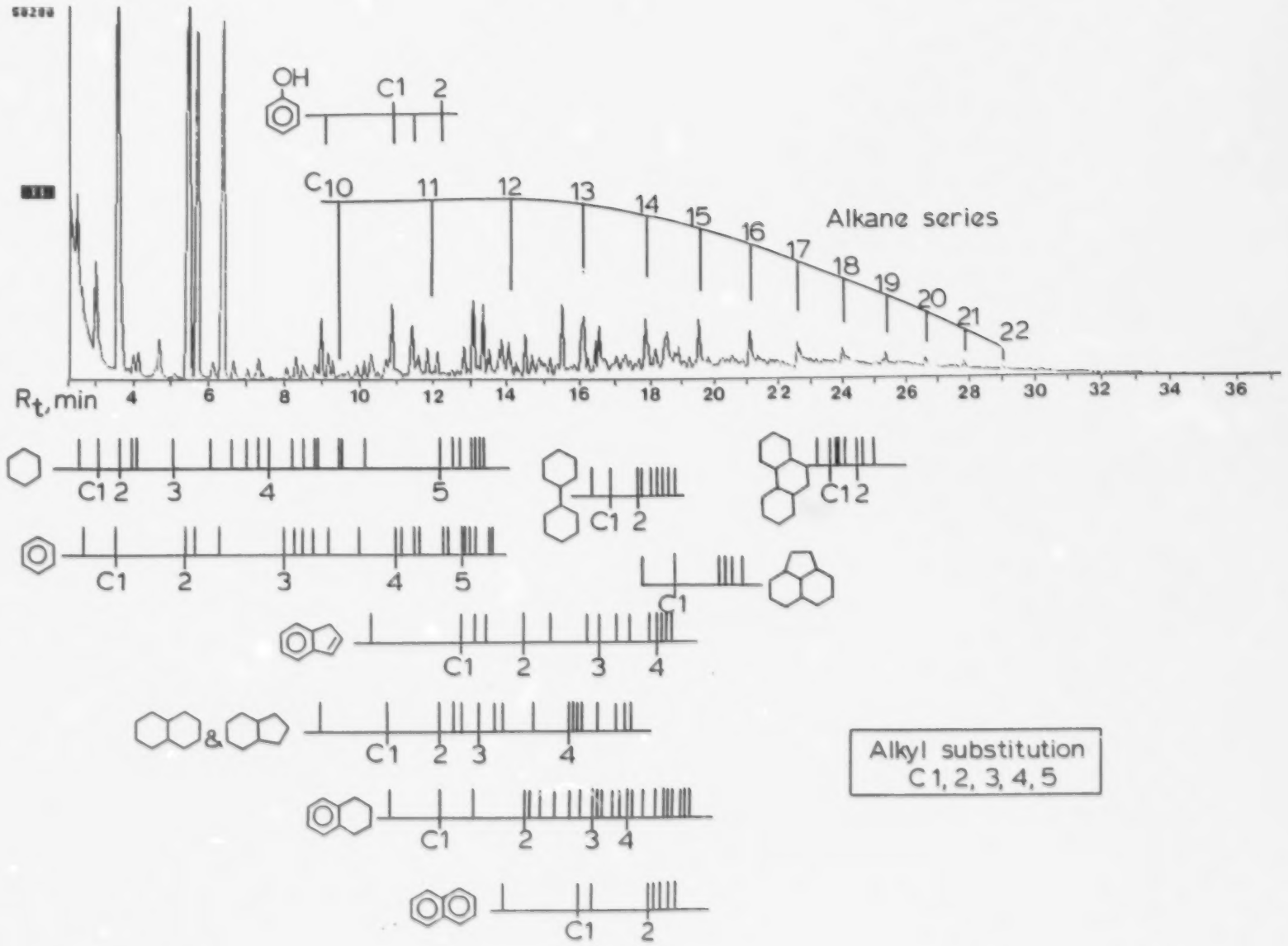
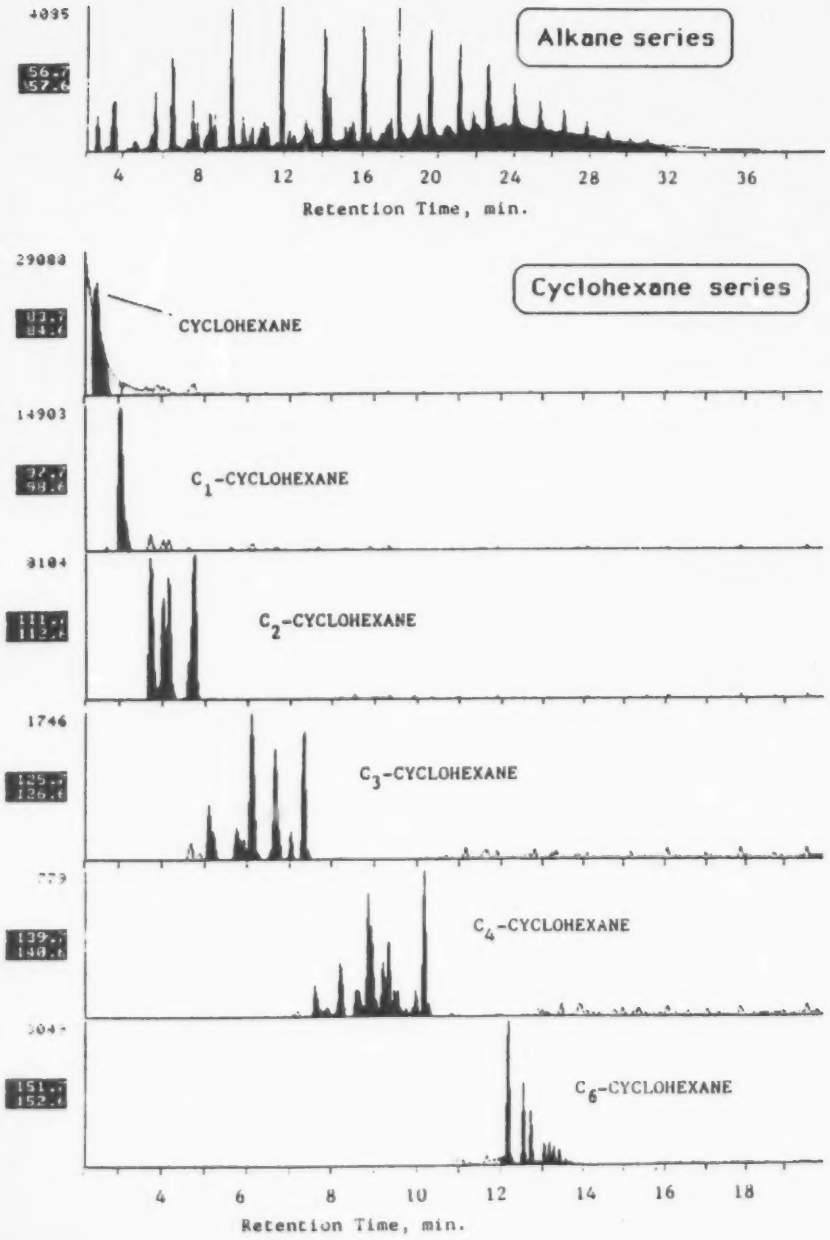
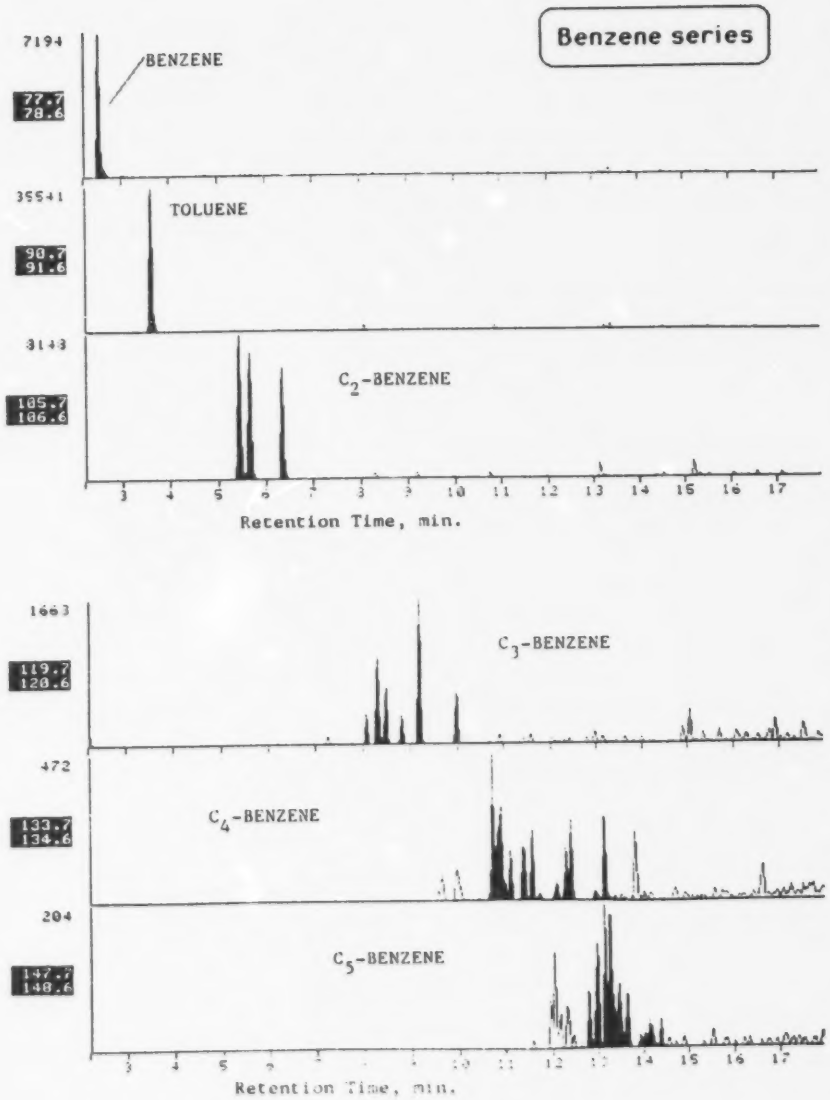


FIGURE 28 SIM OUTPUTS OF HYDROTREATED SAMPLE 06B





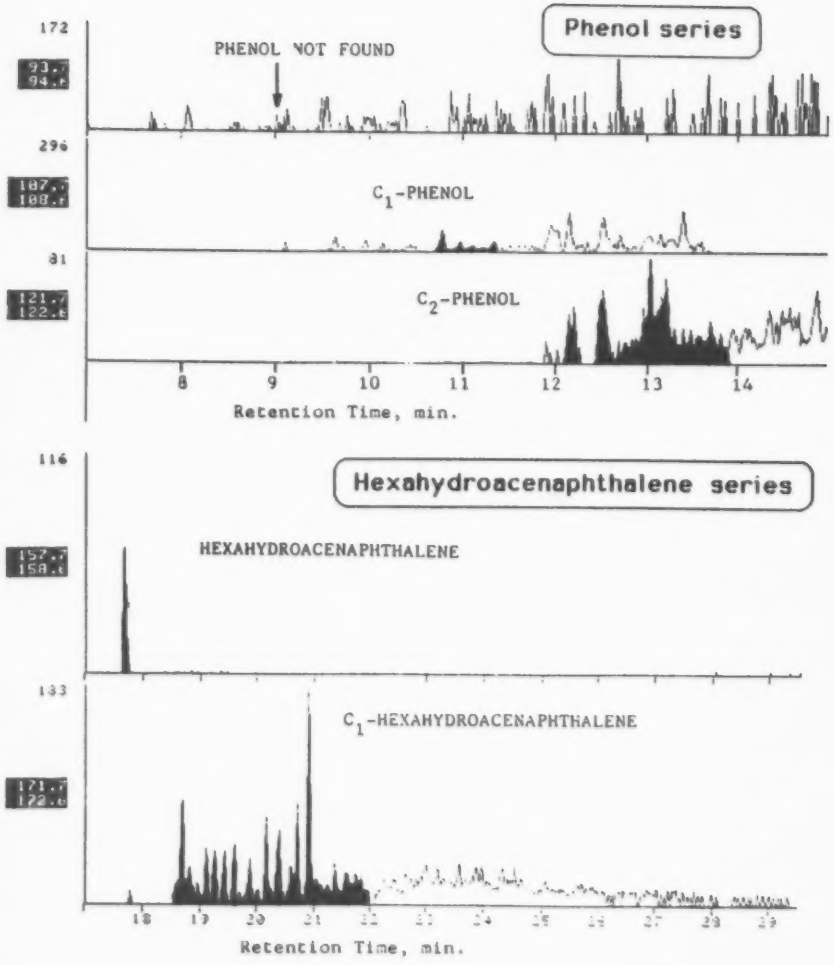


FIGURE 28 (CONTINUED)

SIM OUTPUTS OF HYDROTREATED SAMPLES 06B

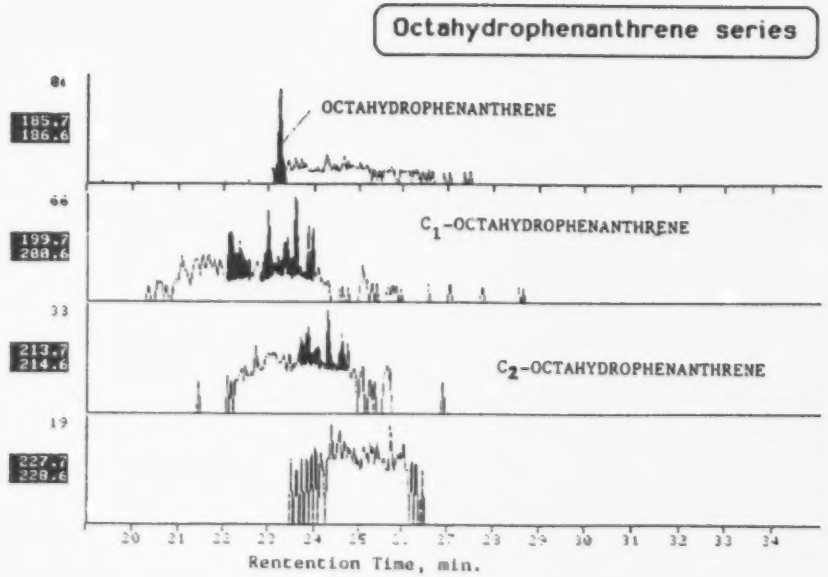
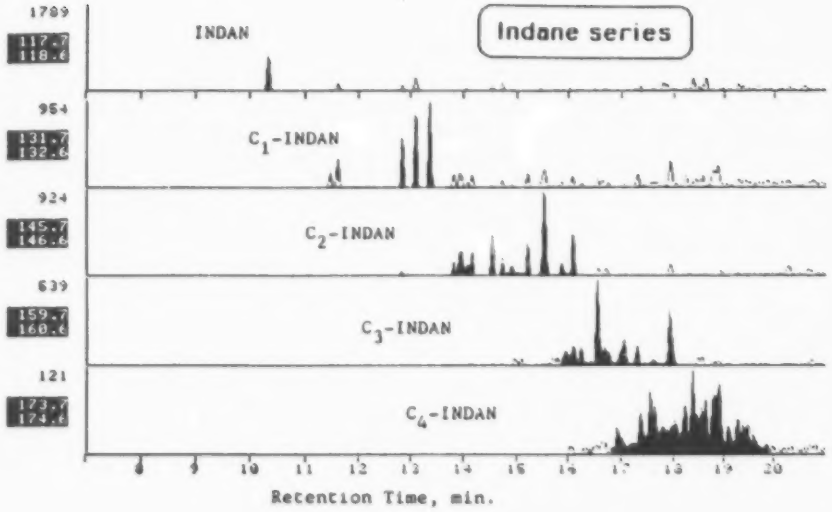
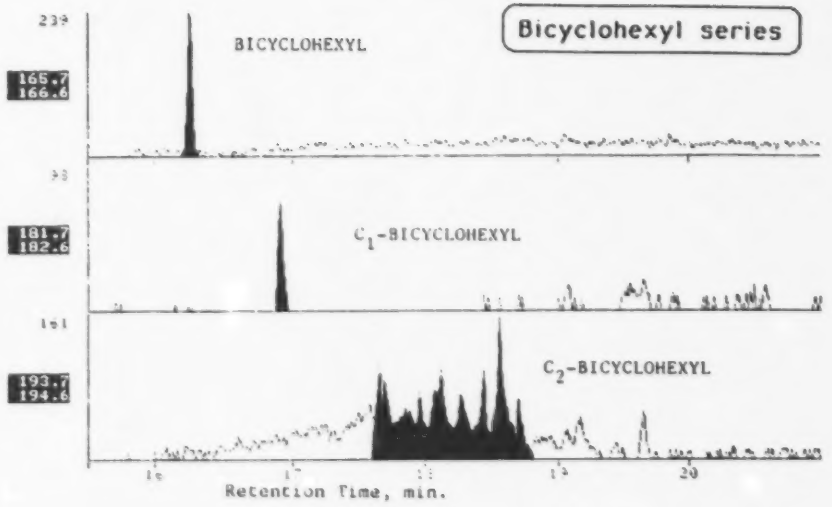
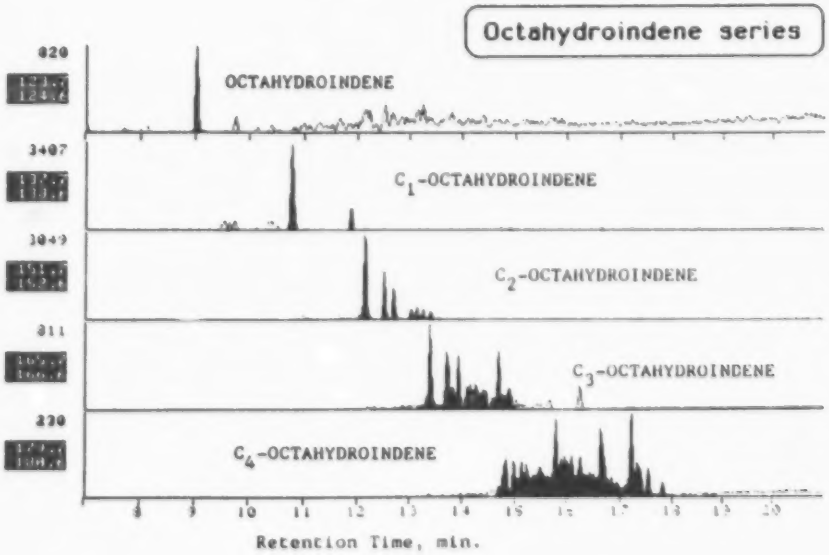


FIGURE 28 (CONTINUED) SIM OUTPUTS OF HYDROTREATED SAMPLES 06B







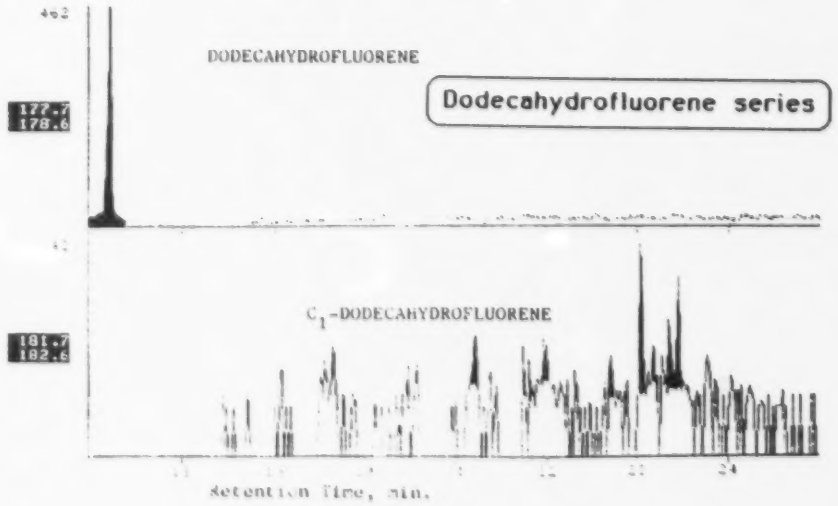


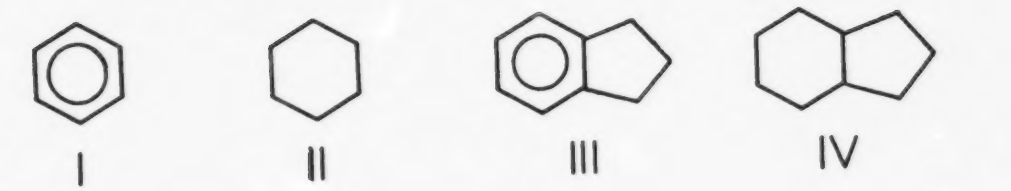
TABLE 16

HYDROCARBON GROUP TYPE AND RELATED COMPOUND CLASSES FOUND IN THE HYDROTREATED DEVCO COAL DISTILLATE SAMPLES

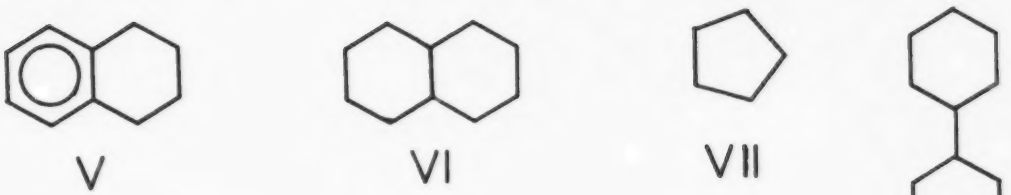
Molecular[(a)] Structure	Hydrocarbon or Compound Group/Type	Molecular Formula of Parent Compound	Molecular Weight of Alkyl Substitution					
			nil	C_1	C_2	C_3	C_4	C_5
-	Alkanes	C_nH_{2n+2}	(to $C_{32}H_{66}$)					
I	Benzenes	C_6H_6	78	92	106	120	134	148
II	Cyclohexanes	C_6H_{12}	84	98	112	126	138	152
III	Indans	C_9H_{10}	118	132	146	160	174	-
IV	Octahydroindenes	C_9H_{16}	124	138	152	166	-	-
V	Tetrahydronaphthalenes	$C_{10}H_{12}$	132	146	160	174	188	-
VI	Decahydronaphthalenes	$C_{10}H_{18}$	138	152	166	180	194	-
VII	Cyclopentanes	C_5H_{10}	70	84	98	-	-	-
VIII	Bicyclohexyls	$C_{12}H_{22}$	166	180	194	-	-	-
IX	Dodecahydrofluorenes	$C_{13}H_{22}$	178	192	206	-	-	-
X	Hexahydroacenaphthalenes	$C_{12}H_{14}$	158	172	186	-	-	-
XI	Octahydrophenanthrene, anthracenes	$C_{14}H_{18}$	186	200	214	228	-	-
XII	Phenols	C_6H_6O	94	108	122	136	150	164
XIII	Bicyclo-alkanes		(e.g. [2.2.1],[3.2.1] etc.)					
XIV	Polynuclear aromatic hydrocarbons (2-3 ring): See Table 11.							

(a) On the following page.

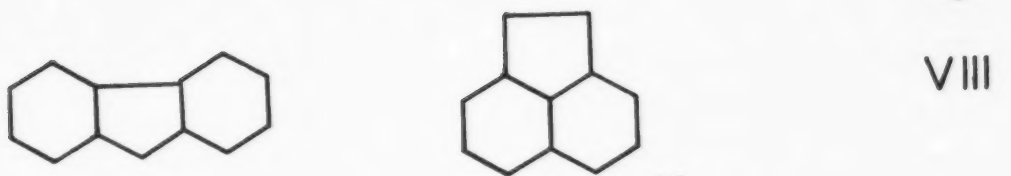
TABLE 16 (continued)



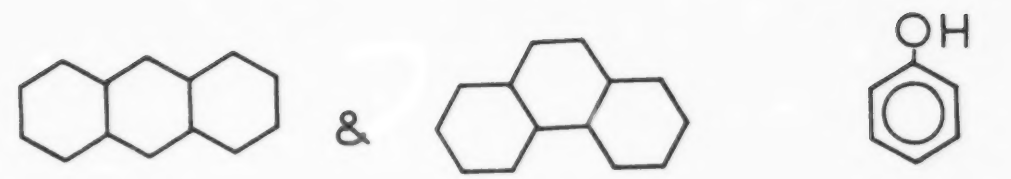
I II III IV



V VI VII VIII



IX X



XIa & XIb XII

[2.2.1] [3.3.1]

XIII

TABLE 17

HYDROGENATED NITROGEN HETEROCYCLES FOUND IN THE HYDROTREATED DEVCO COAL DISTILLATE SAMPLES

No. of Ring[a]		Molecular Formula of Parent Compound	Molecular Weight of Alkyl Derivative			
			nil	C_1	C_2	C_3
	2-Ring System:					
I	Quinoline and/or isoquinolines	C_9H_7N	129	143	157	171
II	Tetrahydro-compounds	$C_9H_{11}N$	133	147	161	175
III	Hexahydro-compounds	$C_9H_{13}N$	135	149	163	177
IV	Decahydro-compounds	$C_9H_{17}N$	139	153	167	181
	3-Ring System:					
V	Acridines	$C_{13}H_9N$	179	193	207	-
VI	Dihydro-compounds	$C_{13}H_{11}N$	181	195	209	-
VII	Tetrahydro-compounds	$C_{13}H_{13}N$	183	197	211	-
VIII	Hexahydro-compounds	$C_{13}H_{15}N$	185	199	213	-
IX	Octahydro-compounds	$C_{13}H_{17}N$	187	201	-	-
X	Decahydro-compounds	$C_{13}H_{19}N$	189	203	-	-

(a) Hydrogenated compounds are referred to the two key parent compounds I or V; see Table 11 for structural formula.

FIGURE 29

SIM OUTPUTS OF HYDROGENATED N-CONTAINING SPECIES IN HYDROTREATED LIQUID SAMPLE #6B

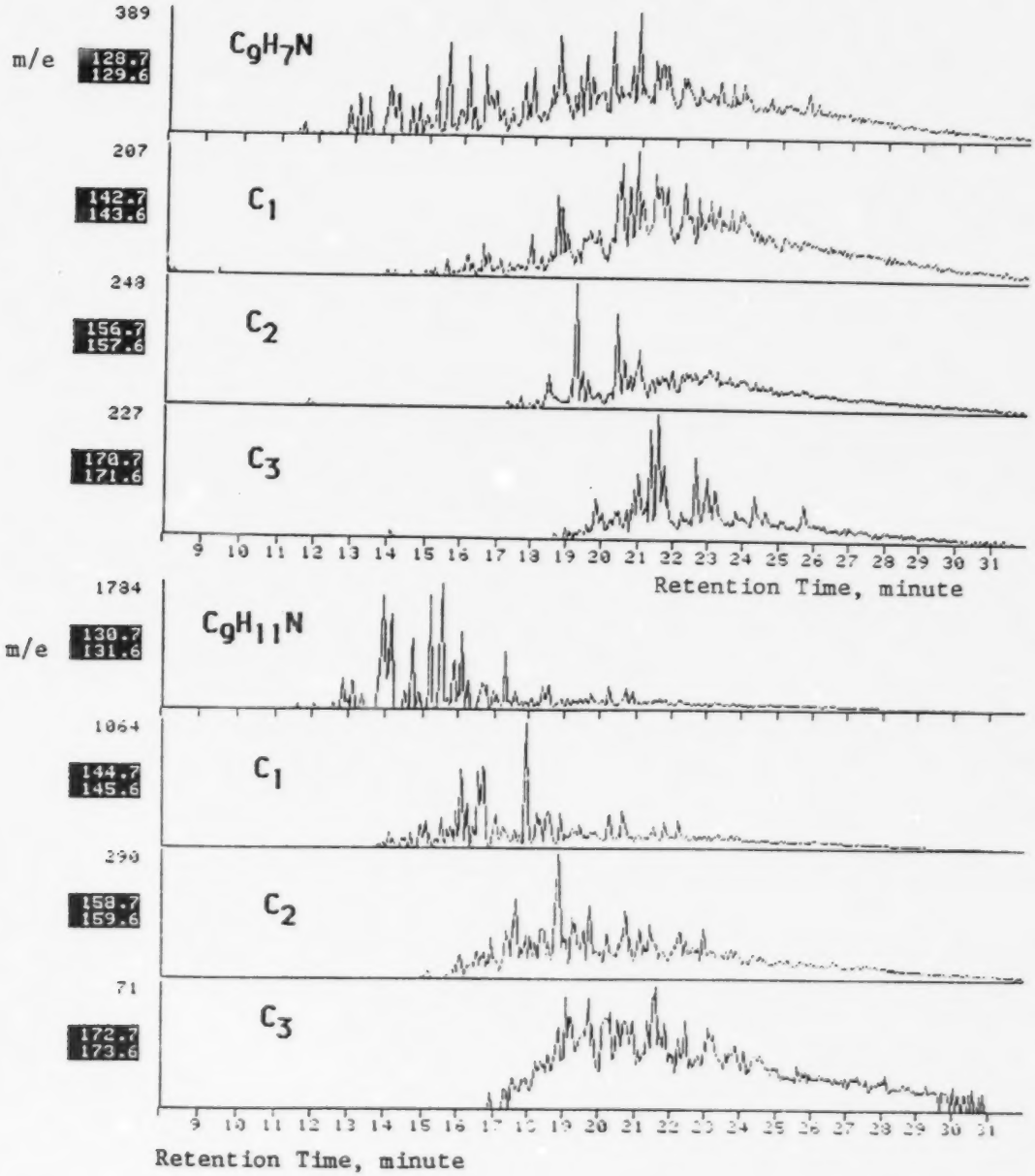


FIGURE 29 (continued)

SIM OUTPUTS OF HYDROGENATED N-CONTAINING SPECIES IN HYDROTREATED LIQUID SAMPLE #6B

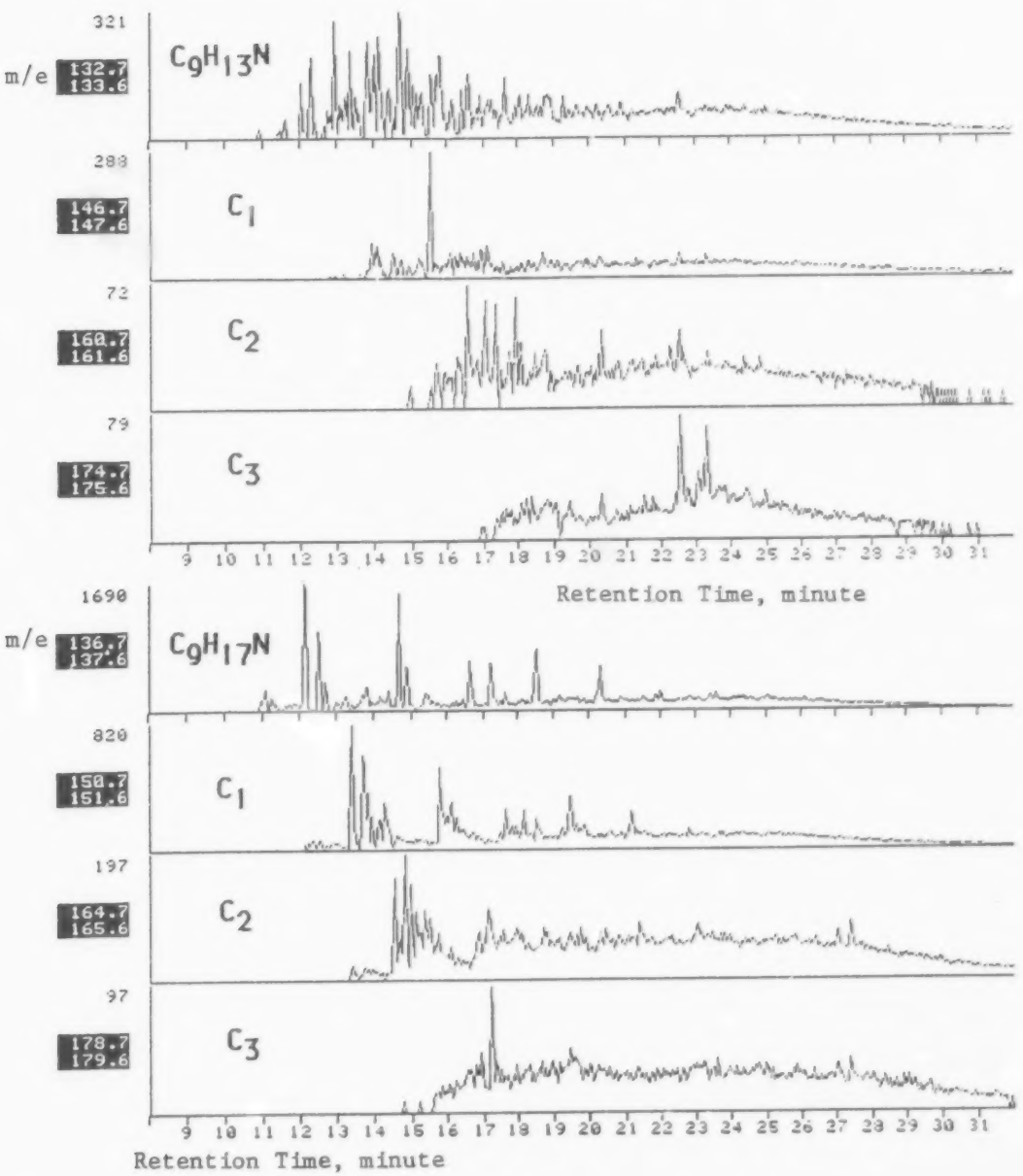


FIGURE 29 (continued)

SIM OUTPUTS OF HYDROGENATED N-CONTAINING SPECIES IN HYDROTREATED LIQUID SAMPLE #68

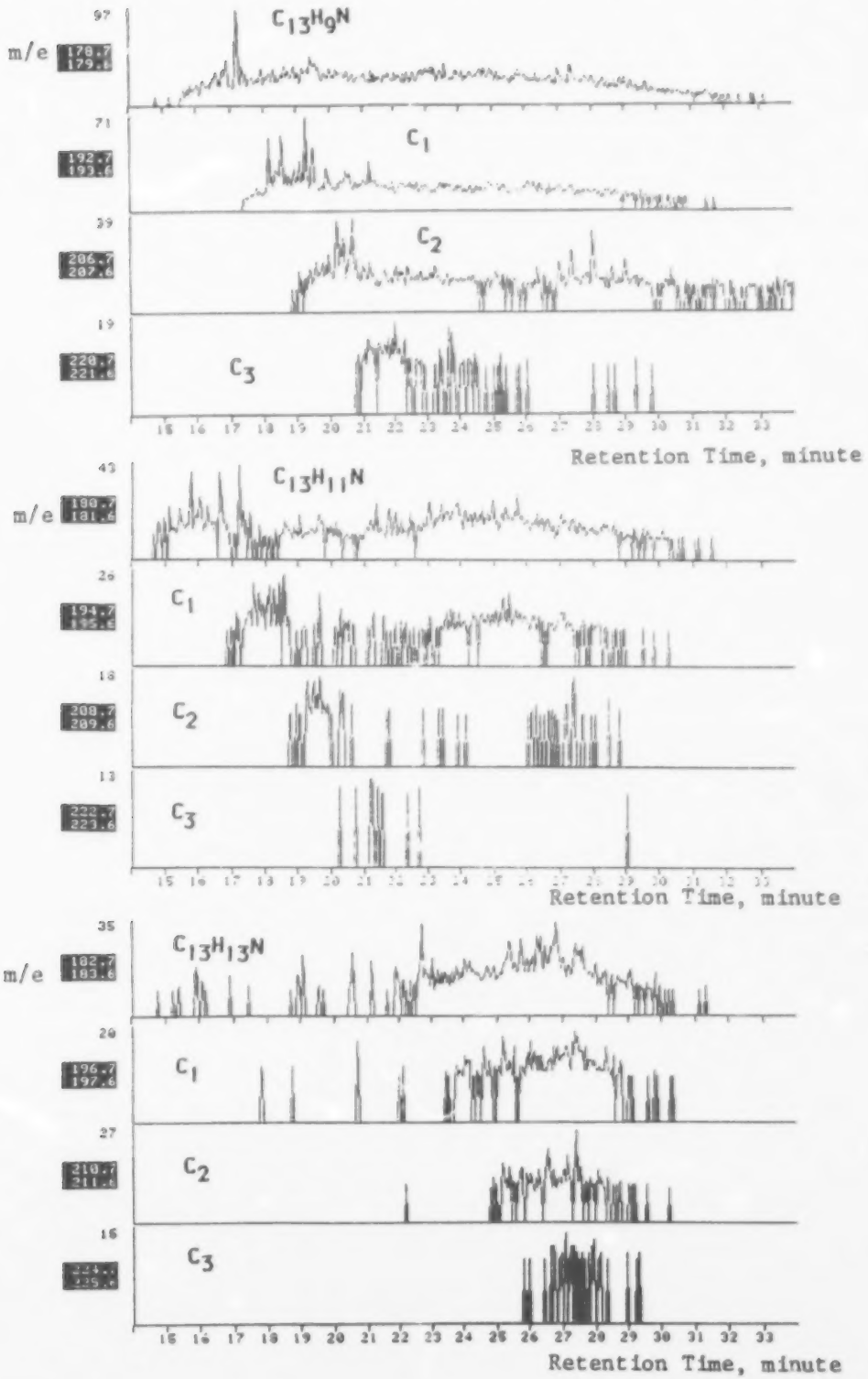
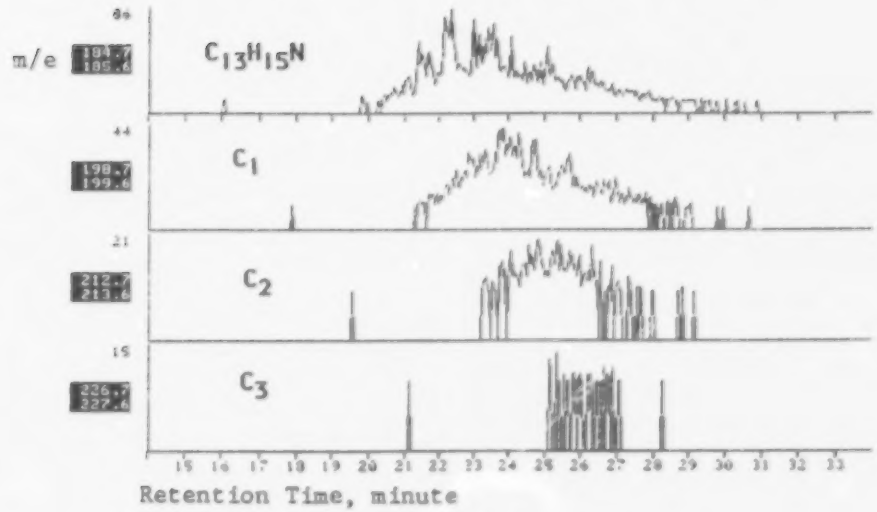
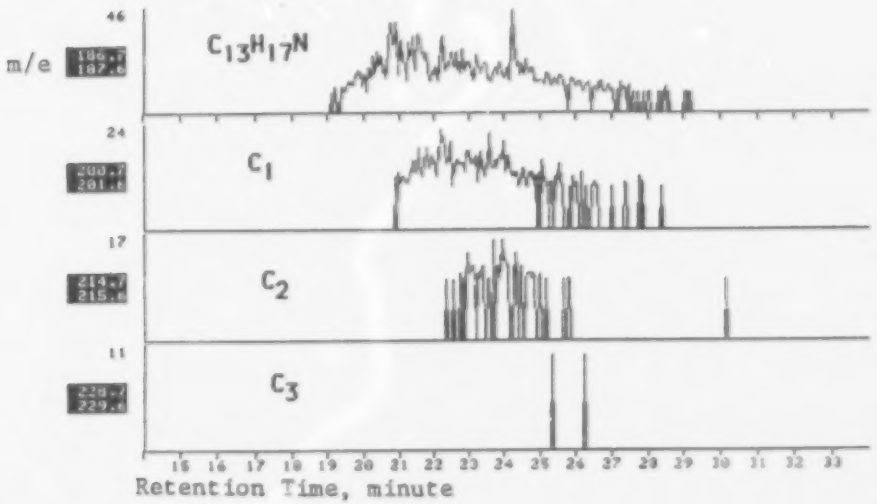


FIGURE 29 (continued)

SIM OUTPUTS OF HYDROGENATED N-CONTAINING SPECIES IN HYDROTREATED LIQUID SAMPLE #68





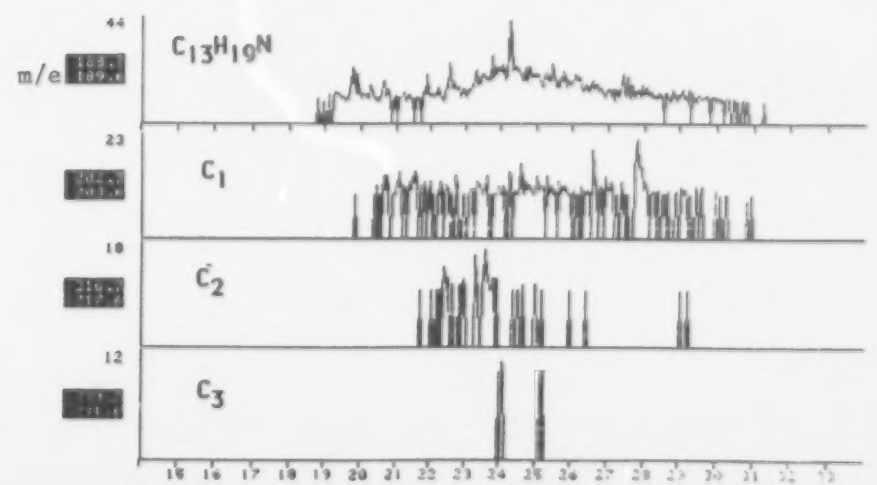


TABLE 18

HYDROCARBON GROUP TYPE CLASSIFICATION OF HYDROTREATED DEVCO TAR DISTILLATE

Hydrocarbon Group Type	Hydrotreating Experiment No.								
	6B	6C	6D	6E	6F	6G	6H	6I	6J
Alkanes (a)	15.5	13.5	10.8	11.6	11.1	14.0	9.6	13.1	11.1
Cyclohexanes	32.1	17.4	14.8	14.0	17.3	7.1	5.9	10.4	6.8
Benzenes	13.5	36.9	42.3	38.5	40.0	46.1	54.9	40.1	52.3
Indans (b)	3.3	3.0	2.7	3.1	3.3	1.8	1.7	3.3	1.8
Octahydroindenes	1.0	0.6	0.6	0.5	0.6	0.2	0.5	0.5	0.3
Naphthalenes	4.3	3.6	3.2	3.7	2.8	4.7	4.5	4.6	3.4
Tetrahydronaphthalenes	1.6	3.7	3.2	3.5	3.3	2.2	2.1	3.3	2.7
Decahydronaphthalenes	3.1	2.3	2.2	2.1	2.7	2.0	2.4	2.6	2.6
Cyclopentanes	1.6	1.0	0.8	0.5	1.1	~0	0.2	0.9	1.4
Other identified H.C.s (c)	10.1	5.7	6.7	8.1	6.4	7.1	7.1	6.8	5.8
Phenols	3.8	3.8	3.7	4.1	4.5	3.4	2.5	4.4	2.8
Other oxygen cpds (d)	1.6	1.2	0.8	1.8	1.9	1.0	1.1	2.5	1.6
Nitrogen compounds (e)	0.2	0.4	0.5	0.3	0.2	1.8	1.4	1.0	1.2
Total Accountable Components	91.7	93.1	92.3	91.8	95.2	91.4	93.9	93.5	93.8

(a) Including normal and branched alkanes.
(b) Also known as 2,3-dihydro-1H-indene.
(c) Including bicyclohexyls, bicyclo-alkanes, C7 to C9-cycloalkanes, spiro-alkanes, and non or partially hydrogenated fluorenes, acenaphtylenes, phenanthrenes, etc.
(d) Including substituted furans, benzofurans, dibenzofurans, ketones and oxo-compounds.
(e) Including partially hydrogenated compounds derived from quinolines, isoquinolines, and acridines.

molecular weight 160, the 0.32%S can be converted into an equivalent amount of 1.75% sulphur compounds in the virgin liquid. All hydrotreated liquids contain less than 0.09%S. Perhaps the lack of positive identification of sulphur containing species is that the compounds belong to entirely different homologs than were investigated. This is clearly an area where further work should be done.

5.5 Comparison of virgin liquid and hydrotreated samples

Table 19 recapitulates the changes in elemental composition between the virgin liquid and two hydrotreated samples 6B and 6E. The virgin liquid is lower in hydrogen content than the averge of the two hydrotreated samples (7.96 versus 12.2 percent), higher in oxygen content (5.92 percent versus 0.1 percent), higher in nitrogen content (1.4 percent versus 0.3 percent) and higher in sulphur content (0.35 percent versus 0.03 percent). The atomic H/C ratio increases upon hydrotreating from 1.12 to 1.53 - 1.83.

Table 20 presents data from Tables 15 and 18 reconstituted into eight major groups to provide a further comparison. The effectiveness of the hydrotreating can be shown from the relative amounts of saturated/unsaturated homologs, and the reduction in heteroatomic species between the virgin liquid and the hydrotreated samples.

Comparison of the virgin liquid and hydrogenated sample 6B (Tables 19 and 20) shows:

1. Nitrogen and sulphur species present in the virgin liquid were removed to about 85%.

2. Oxygenated species were more difficult to remove. Only about a 40% reduction was evident.

3. All alkenes were hydrogenated.

4. Seventy percent of the benzenes were converted to respective cyclohexanes.

5. Thirty percent of naphthalenes were converted into tetrahydro and dodecahydronaphthalenes.

Some cyclohexanes and hydronaphthalenes might have been produced from heteroatomic species eg. via ring cleavage hydrogenolysis such as hydrodenitrogenation.

The apparent reduction in aliphatic hydrocarbon yield might be due to losses of lighter saturated species during the hydrotreating process and handling of liquids.

Comparison of the liquid structure of samples 6B and 6E (Table 20) shows basic resemblance of the structure with marginal differences in bicyclic C_{12} hydrocarbon content and heteroatomic species content. A remarkable difference is found in the weight ratio of benzenes/cyclohexanes. While the hydrotreating conditions were basically similar (Table 8) except for a minor feed rate change, the gas yield for 6B was about 3.9 times higher than for 6E, with CH_4, C_2H_6 and C_3H_8 being factors of 1.9 and 2.4 and 5.7 respectively.

6. SUMMARY AND CONCLUSIONS

1. Devco coal of particle size 0.7-1.7 mm was pyrolyzed in nitrogen in a 12.8 cm dia. atmospheric pressure spouted bed pyrolyzer at a temperature of 670°C fed at 0.9 kg coal/h. The raw tar yield was about 26% and the tar recovery about 21 wt.% of coal fed. The raw tar analyzed 84.1% C, 8.0% H, 1.33% N, 9.9% S and 7.1% O.

2. The raw tar was separated by short path distillation into two liquid fractions - Fractor #1 (IBP-110°C) and Fraction 2 (110-390°C), and a solid residue. Recoveries were 2.6%, 62.1% and 35.3% respectively. Fraction 2 had an elemental composition similar to the raw tar except that sulphur and oxygen were slightly decreased to 0.35% and 5.9% respectively while the carbon content was increased.

3. Fraction #1 (IBP-110oC) showed about 80 chromatographic peaks. Some 90 wt.% of the liquid was identified. This fraction was dominated by alkylbenzenes (64%), phenols (10%), and normal and branched alkanes and alkenes (7.6%). Fraction 2 (110-390°C) showed about 130 chromotographic peaks. Eighty-three weight percent of this fraction was identified as 109 different compounds. Dominant species were alkylbenzenes (41%), normal and branched alkanes and alkenes (21%), naphthalenes (6.5%) and phenols (6.3%).

4. Distillate Fraction #2 was subjected to hydrotreating at Saskatchewan Research Council under a range of severities, using a commercial Ni-Mo hydrotreating catalyst at 360 and 380°C and LHSV of 0.4 to 1.1 hr^{-1}. Under the highest hydrogen pressures (~18 MPa), oxygen was reduced from 5.92 to below 0.1%, sulphur from 0.35 to about 0.05%, and nitrogen and hydrogen contents of the hydrotreated liquids are correlated with H_2 consumption.

TABLE 19

COMPARISON OF ELEMENTAL ANALYSIS
OF VIRGIN AND HYDROTREATED SAMPLES

	Virgin Liquid	Sample 6B	Sample 6E
Wt. % C	84.80	86.65	88.70
H	7.96	13.23	11.30
N	1.41	<0.3	<0.3
S	0.35	0.06	0.01
O	5.92	~0.0	(-0.0)
TOTAL	100.44	99.94 (a)	100.01 (a)
H/C Atomic Ratio	1.12	1.83	1.53

(a) Not including nitrogen content.

TABLE 20

COMPARISON OF HYDROCARBON GROUP TYPE OF
VIRGIN LIQUID AND HYDROTREATED SAMPLES 6B AND 6E

Hydrocarbon (H.C.) derivative group / Type	Weight % distribution in sample		
	Virgin Liquid (a)	6B	6E
1. n-and branched alkanes	17.4	15.5	11.6
Alkenes	3.6	0.0	0.0
Total aliphatic H.C.	21.0	15.5	11.6
2. Monocyclic C_6-H.C.			
Benzenes	40.8	13.5	38.5
Cyclohexanes	0.0	32.1	14.0
Total C_6-H.C.	40.8	45.6	52.5
3. Bicyclic C_{12}-H.C.			
Naphthalenes	6.5	4.3	3.7
Hydronaphthalenes (b)	0.0	4.7	5.6
Total C_{12}-H.C.	6.5	9.0	9.3
4. Oxygenated compounds:			
Phenols	6.3	3.8	4.1
Others (c)	2.5	1.6	1.8
Total oxy-compounds	8.8	5.4	5.9
5. Nitrogen compounds (d)	1.50	0.2	0.3
6. Sulphur compounds (e)			
N.I.	est. 1.75	est. 0.3	est. 0.05
7. Total heteroatomic compounds			
Items 4 + 5 + 6	12.1	5.9	6.3
8. All others H.C.	4.4	16.0	12.2
Total accountable	84.9	92.0	91.9

(a) The tar distillate fraction Fr#2 (110 - 390°C).
(b) Hydronaphthalenes: tetrahydro- and decahydronaphthalenes.
(c) Including benzofurans, dibenzofurans, oxo-compounds, etc.
(d) Including quinolines, carbazoles and their respective hydrogenated intermediates.
(e) Sulphur compounds were not identified (N.I.); the sulphur contents were found to be 0.35, 0.06 and 0.01 for virgin, 6B and 6E respectively; assuming average moleculcur weight of 160 (i.e. 20% sulphur content).

7. FUTURE WORK AND COMMENTS

There is room to improve the trapping method and efficiency for the coal tar vapor generated from the existing pilot pyrolysis unit.

The coal tar as obtained from the rapid pyrolysis of Devco coal is characterized by its high boiling range and low H/C atomic ratio (cf. 1.12). Although the refining of the hydrotreating conditions and the further downstream upgrading of these hydrotreated liquids was not considered within the scope of this study, a few fundamental facts should be noted:

1. Raw tar may have to be subjected to visbreaking or mild hydrotreating at the pyrolysis site to improve its handling characteristics.

2. High nitrogen (1.4%) and oxygen (5.9%) contents and low sulphur content (0.4%) of the middle-distillate might have to subject to mild hydrotreating first using cobalt-type hydrotreating catalyst prior to severe hydrotreating using Ni-Mo catalyst.

3. R&D is required on the refining processes, including the possibility of removal of nitrogen containing material prior to the hydroprocessing.

4. Fundamental research is required for a better understanding of hydrodenitrogenation and hydrodeoxygenation catalysis and the reaction mechanisms as well as the development of improved and new catalysts.

5. Research is required for the complete characterization of the char product from the pyrolysis process to lead the way for its best utilization (e.g. gasification or combustion).

6. **Characterization of the asphaltene reduction under different hydrotreating conditions as well as the distillation characteristics of the hydrotreated liquids are essential for a complete evaluation of this hydrotreating study. Furthermore, the presence of certain elements such as V, Cd, Cr, etc. might be determined.**

5. The hydrotreated samples were subjected to detailed chemical characterization. All hydrotreated samples were found to have similar compositional homologs with the amounts and distributions depending on the hydrotreating conditions. Major remaining nitrogen-containing homologs were hydrogenated quinolines and isoquinolines, which were typically present at the 0.3% level or less in liquids of highest severity treating. Phenols were present at the 2.5-4.5% level compared to 6.3% in the untreated fraction, and were accompanied by furans and ketones. Sulphur species could not be identified.

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2. K.C. Teo, A.P. Watkinson and D.J. Jung, "Characterization of Liquid Fuels from Spouted Bed Pyrolysis of Canadian Coals," DSS File No. 20SU 23440-2-9093; Final Report July, 1984.

3. M.F. Ali, M. Hasan, A. Bukhari and M. Saleem, Oil and Gas Journal, page 71-77; Aug 12, 1975.

4. S.E. Scheppele, G.J. Greenwood, R.J. Pancirov and T.R. Ashe, "Chemical Composition of Raw and Upgraded Anthracene Oil and the Chemistry of Coal Liquids Upgrading", Chapter 2 in "Upgrading Coal Liquids", ed. by R.F. Sullivan, ACS Symposium series 156, ACS, Washington, D.C., 1981.

LETTER FROM SASKATCHEWAN RESEARCH COUNCIL CONCERNING THE PROBLEM OF DEACTIVATION OF HYDROTREATING CATALYST

PETROLEUM DIVISION

Saskatchewan
Research Council 5'5 Henderson Drive Regina Sask Canada S4N 5X1 Phone (306) 787-9400 Telecopy 949-2644

October 30, 1986

Dr. Kc Teo
Department of Chemical Engineering
University of British Columbia
2216 Main Mall
Vancouver, B.C.
V6T 1W5

Dear Dr. Teo:

Re: Hydrotreating of Coal Liquids

This letter is in response to our telephone conversations regarding the deactivation of the catalyst used in the coal hydrotreating experiments.

SRC's experience with the Shell S-424 catalyst has shown it to be very effective in typical hydrotreating applications. We recently used the catalyst to do some hydrotreating of a partially upgraded synthetic gas oil. The catalyst has been tested for runs 140, 190 and 504 hours on stream time. The longest run showed that the catalyst was initially highly active with a relatively immediate deactivation (within 48 hours of start-up) to a plateau. Over the remaining period no significant deactivation occurred.

When the coal liquids were hydrotreated the run length was not long enough to normally cause any deactivation. The only possible deactivation could have been caused by coke formation on the catalyst. This can be determined by performing surface area, pore size distribution and carbon analysis on the used catalyst. The catalyst should be extracted with tetrahydrofuran (THF) prior to analysis. For reference, the catalyst from the previously mentioned 504 hour test had a 10% reduction in surface area (when compared to fresh catalyst) and a 4% carbon content with a minor reduction in activity. Coke formation can also be detected by an increasing pressure drop across the catalyst bed. No significant pressure drop was measured across the bed during the coal liquid runs.

Hydrogen consumption and light gas production can be another sign of catalyst deactivation and coke deposition on the catalyst. Gas make and hydrogen consumption maintained expected values after changes in operating conditions were made.

. . 2

The other question you raised was when equilibrium was achieved during the coal experiments. Past experience has shown that equilibrium was achieved after about an hour after changes were made to the conditions. This was determined from gas product analysis. It does take longer to establish equilibrium when starting the unit up, however, once initial equilibrium is achieved it is quickly re-established after any change to the operating conditions. In this case the unit was started up and the experiments for the high pressure series were completed non-stop. It was intended to continue on with the low pressure series but the unit proved unoperable at those conditions. The low pressure series was completed after operating conditions were modified so that the unit would operate smoothly.

A catalyst analysis is really the only way to determine if the catalyst did significantly deactivate. I can provide no more insight into the success of the hydrotreating without a catalyst analysis.

I trust this is sufficient for the purposes of your report. If you require further clarification, please do not hesitate to contact me.

Yours truly,

D W Soveran

Douglas W. Soveran
Senior Research Engineer
Petroleum Research Unit

DWS/dh

c.c. R. Ranganathan

Saskatchewan
Research Council
PETROLEUM DIVISION

APPENDIX A

PROJECT REPORT - HYDROTREATING OF COAL LIQUIDS

1. Three - one litre bottles labelled Devco Coal Tar were received at SRC on January 6, 1986.

2. A sample was submitted to Analytical Services for a simulated distillation to determine the amount of material boiling in the 110-390°C range. The tar was dissolved in carbon disulphide, then centrifuged to remove any solids. There was sufficient undissolved material remaining that the injection needle plugged when the first analysis attempt was made. The sample was centrifuged again and then injected successfully.

   The analysis revealed that approximately 15% of the sample was THF (tetra hydrofuran).

3. The tar was then loaded into a 5 litre pot in a BR spinning band apparatus. The THF was distilled off at atmospheric pressure. It was intended that the complete distillation to provide a 110-390°C fraction be done in the spinning band column. Dr. Teo advised that a significant amount of the tar would pyrolyze if the spinning band was used and recommended that we use a wiped film evaporator (WFE) distillation unit.

4. The remaining material in the spinning band pot was transferred to the WFE feed flask while still hot (≈140°C). The WFE is a model KDL-4 system manufactured by Leybold-Heraeus.

5. The feed flask was heated to approximately 120°C. The distillation conditions were 160°C evaporator surface temperature and a pressure of 0.25 mmHg. These conditions would yield a cut point of 390°C between the residue and distillate. When the feed was started to the unit the distillate material was flashed off, the remaining residue would not flow under these conditions and as a consequence the roller wipers "froze". The distillation was stopped.

   The equipment was cleaned out using THF, dichromate solution and finally sodium hydroxide solution.

ANALYTICAL SERVICES LAB

ANALYTICAL REPORT

Originator : D. Soveran
Sample Description : Devco Tar #1
Date Received : January 06, 1986
Date Reported : Januar, 29, 1986

A.S. Sample No.: 86-0016
A.S.U. Manager : M. Myers M.E.M. Chemist: E. Chung E C

SIMULATED DISTILLATION BY GAS CHROMATOGRAPHY

VOLUME PERCENT DISTILLED	TEMPERATURE (°C)	VOLUME PERCENT DISTILLED	TEMPERATURE (°C)
IBP	159	55	444
5	235	60	461
10	270	65	476
15	296	70	493
20	320	75	510
25	342	80	530
30	360	85	552
35	378	90	575
40	396	95	603
45	412	FBP	
50	429		

Note: Based on the CS_2 soluble portion of Devco Tar #1.

BOILING RANGE (°C)	VOLUME PERCENT
IBP - 204	2.3
204 - 343	23.0
343 - 525	53.0
525 + Residue	21.7
525 - 600	16.1
600°C + Residue	5.6

AR85-22.1

APPENDIX B

PETROLEUM DIVISION

Saskatchewan
Research Council 515 Henderson Drive Regina, Sask Canada S4N 5X1 Phone (306) 787-9400 Telecopy 949-2644

May 14, 1986

Dr. Kc Teo
Department of Chemical Engineering
2216 Main Mall
University of British Columbia
Vancouver, B.C.
V6T 1W5

Dear Dr. Teo :

Re: Hydrotreating of Coal Liquids

Attached is the remaining experimental data from the hydrotreating of the coal-derived liquids.

Each experiment is summarized by a mass balance, gas analysis, product yield and a description of any operating anamolies that may impact on product qualities.

If you have any questions regarding the data, please do not hesitate to contact me. The catalyst used for the experiments will be forwarded to you shortly. The initially supplied coal tar will also be shipped to you.

Yours truly,

D.W. Soveran
Senior Research Engineer
Petroleum Research Unit

DWS/dh

Attachments

c.c. R. Ranganathan
J. Hutchinson

Experiment No. F86-06A **Date:** April 15, 1986

Feedstock: Suncor Gas Oil with 2.5 wt.% CS

Catalyst : Shell S-424 (a commercial Ni-Mo hydrotreating catalyst)

Reactor Conditions:

Step	LHSV (1/hr)	Pressure (MPA)	Temp. (°C)	Duration
1	1.5	3.0	100	3 hr
2	1.33	3.0	250	6 hr
3	1.33	3.0	300	12 hr
4	1.33	3.0	320	6 hr

Comments: This experiment is performed to change the catalyst from the oxide form to the sulphide form (the higher activity form).

Gas Analysis: No analysis was performed for the presulphiding treatment.

Date: April 22, 1986

Experiment No. F86-068

Feedstock: Devco Coal Tar

Catalyst : Sulphided Shell S-424

Reactor Conditions:

1. Temperature: 360°C
2. Pressure: 17.9 MPa
3. Liquid Feed Rate: 10.5 g/hr
4. Hydrogen Rate: 250 cc/min (@15°C, 1 atm)
5. Duration: 4 hours

Mass Balance:

Liquid Feed: 42 g
Liquid Product: 41.3 g
Liquid Yield: 98.3 % wt. of fresh feed

Gas Volume: 15.2 litres (@ 15°C, 1 atm)
Hydrogen Consumption: 0.0459 g mol/g feed
Gas Yield, (Hydrogen free): 2.75 % wt. fresh feed

Gas Analysis: see following page

Comments: Problems were encountered with the scale for the feed vessel at the beginning of the run, the total amount fed to the unit is estimated from the last three hours of operation.

To calculate the LHSV (Liquid Hourly Space Velocity) it is necessary to know the density of the feedstock. To calculate the LHSV for the reaction system use the following formula.

$$\text{LHSV} = \frac{\text{Feed Rate (g/hr)}}{\text{Density (g/cc) (@ 15°C)} \times 30 \text{ cc (reactor volume)}}$$

ANALYTICAL SERVICES LAB

ANALYTICAL REPORT

Container Identity : Gas Tight Syringe
Continuous Unit Run #: F86-068
Originator : Doug Soveran
Sample Name :
Sample Description : Gas Product
Date Received : April 22, 1986
Date Reported : April 22, 1986

A.S. Sample No.: 86-0747
A.S.U. Manager : M. Myers M.E.M. Chemist: E. Chung

NORMALIZED (ASSUMING AIR FREE)

COMPONENTS	MOLE FRACTION	COMPONENTS	MOLE FRACTION
Methane	0.0265	Methyl-Acetylene	
Ethane	0.0071	cis-2-Butene	
Ethylene		1,3-Butadiene	
Acetylene		i-Pentane	0.0005
Propane	0.0026	n-Pentane	0.0004
Propylene		C_6+	0.0015
Propadiene		Carbon Dioxide	
i-Butane	0.0009	Carbon Monoxide	
n-Butane	0.0075	Hydrogen	0.9417
1-Butene		Nitrogen	0.0063
i-Butylene		Oxygen	
trans-2-Butene		Hydrogen Sulfide	0.0049

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Experiment No. F86-06C **Date:** April 22, 1986

Feedstock: Devco Coal Tar

Catalyst : Sulphided Shell S-424

Reactor Conditions:

1. Temperature: 360°C
2. Pressure: 18.0 MPa
3. Liquid Feed Rate: 28.0 g/hr
4. Hydrogen Rate: 500 cc/min
5. Duration: 4 hours

Mass Balance:

Liquid Feed: 112 g
Liquid Product: 111.0 g
Liquid Yield: 99.1 % wt. of fresh feed

Gas Volume: 43.4 litres (@ 15°C, 1 atm)
Hydrogen Consumption: 0.0295 g mol/g feed
Gas Yield, (Hydrogen free): 2.67 % wt. fresh feed

Gas Analysis: see following page

Comments: A relatively trouble free and stable experiment

ANALYTICAL SERVICES LAB

ANALYTICAL REPORT

Container Identity : Gas Tight Syringe
Continuous Unit Run # : F86-06C
Originator : Doug Soveran
Sample Name :
Sample Description : Gas Product
Date Received :
Date Reported : April 25, 1986

A.S. Sample No.: 86-0748A
A.S.U. Manager : M. Myers M.E.M. Chemist: E. Chung E.C

NORMALIZED (ASSUMING AIR FREE)

COMPONENTS	MOLE FRACTION	COMPONENTS	MOLE FRACTION
Methane	0.0100	Methyl-Acetylene	
Ethane	0.0049	cis-2-Butene	
Ethylene	Trace	1,3-Butadiene	
Acetylene		i-Pentane	0.0002
Propane	0.0064	n-Pentane	0.0003
Propylene		C_6+	0.0032
Propadiene		Carbon Dioxide	Trace
i-Butane	0.0007	Carbon Monoxide	0.0004
n-Butane	0.0096	Hydrogen	0.9606
1-Butene		Nitrogen	0.0028
i-Butylene		Oxygen	
trans-2-Butene		Hydrogen Sulfide	0.0009

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Experiment No. F86-06D **Date:** April 22, 1986

Feedstock: Devco Coal Tar

Catalyst : Sulphided Shell S-424

Reactor Conditions:

1. Temperature: 380°C
2. Pressure: 17.7 MPa
3. Liquid Feed Rate: 29.0 g/hr
4. Hydrogen Rate: 500 cc/min
5. Duration: 4 hours

Mass Balance:

Liquid Feed: 116 g
Liquid Product: 106.8 g
Liquid Yield: 92.1 % wt. of fresh feed

Gas Volume: 52.86 litres (@ 15°C, 1 atm)
Hydrogen Consumption: .0263 g mol/g feed
Gas Yield, (Hydrogen free): 5.94 % wt. fresh feed

Gas Analysis: see following page

Comments: Another stable and uneventful run.

ANALYTICAL SERVICES LAB

ANALYTICAL REPORT

Container Identity : Gas Tight Syringe
Continuous Unit Run # : F86-06D
Originator : Doug Soveran
Sample Name :
Sample Description : Gas Product
Date Received :
Date Reported : April 25, 1986

A.S. Sample No.: 86-0748B
A.S.U. Manager : M. Myers M.M. Chemist: E. Chung EC

NORMALIZED (ASSUMING AIR FREE)

COMPONENTS	MOLE FRACTION	COMPONENTS	MOLE FRACTION
Methane	0.0281	Methyl-Acetylene	
Ethane	0.0111	cis-2-Butene	
Ethylene		1,3-Butadiene	
Acetylene		i-Pentane	0.0003
Propane	0.0113	n-Pentane	0.0005
Propylene		C_6+	0.0030
Propadiene		Carbon Dioxide	0.0002
i-Butane	0.0010	Carbon Monoxide	0.0006
n-Butane	0.0105	Hydrogen	0.9058
1-Butene		Nitrogen	0.0270
i-Butylene		Oxygen	
trans-2-Butene		Hydrogen Sulfide	0.0007

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Experiment No. F86-06E **Date:** April 22, 1986

Feedstock: Devco Coal Tar

Catalyst : Sulphided Shell S-424

Reactor Conditions:

1. Temperature: 360°C
2. Pressure: 17.9 MPa
3. Liquid Feed Rate: 12 g/hr
4. Hydrogen Rate: 250 cc/min
5. Duration: 4 hours

Mass Balance:

Liquid Feed: 48 g
Liquid Product: 44.6 g
Liquid Yield: 92.9 % wt. of fresh feed

Gas Volume: 25.0 litres (@ 15°C, 1 atm)
Hydrogen Consumption: .0345 g mol/g feed
Gas Yield, (Hydrogen free): 10.6 % wt. fresh feed

Gas Analysis: see following page

Comments: Smooth and uneventful experiment.

ANALYTICAL SERVICES LAB

ANALYTICAL REPORT

Container Identity : Gas Tight Syringe
Continuous Unit Run # : F86-06E
Originator : Doug Soveran
Sample Name :
Sample Description : Gas Product
Date Received :
Date Reported : April 25, 1986

A.S. Sample No.: 86-0749
A.S.U. Manager : M. Myers M.E.M. Chemist: E. Chung EC

NORMALIZED (ASSUMING AIR FREE)

COMPONENTS	MOLE FRACTION	COMPONENTS	MOLE FRACTION
Methane	0.0506	Methyl-Acetylene	
Ethane	0.0173	cis-2-Butene	
Ethylene		1,3-Butadiene	
Acetylene		i-Pentane	0.0005
Propane	0.0149	n-Pentane	0.0008
Propylene		C_6+	
Propadiene		Carbon Dioxide	Trace
i-Butane	0.0012	Carbon Monoxide	0.0003
n-Butane	0.0101	Hydrogen	0.8316
1-Butene		Nitrogen	0.0725
i-Butylene		Oxygen	
trans-2-Butene		Hydrogen Sulfide	0.0003

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Experiment No. F86-06F **Date:** April 23, 1986

Feedstock: Devco Coal Tar

Catalyst : Sulphided Shell S-424

Reactor Conditions:

1. Temperature: 380°C
2. Pressure: 18.1 MPa
3. Liquid Feed Rate: 14.0 g/hr
4. Hydrogen Rate: 250 cc/min
5. Duration: 4 hours

Mass Balance:

Liquid Feed: 56 g
Liquid Product: 51.4 g
Liquid Yield: 91.8 % wt. of fresh feed

Gas Volume: 22.5 litres (@ 15°C, 1 atm)
Hydrogen Consumption: .030 g mol/g feed
Gas Yield, (Hydrogen free): 5.2 % wt. fresh feed

Gas Analysis: see following page

Comments: Smooth and uneventful experiment.

ANALYTICAL SERVICES LAB

ANALYTICAL REPORT

Container Identity : Gas Tight Syringe
Continuous Unit Run # : F86-06F
Originator : Doug Soveran
Sample Name :
Sample Description : Gas Product
Date Received :
Date Reported : April 25, 1986

A.S. Sample No.: 86-0750
A.S.U. Manager : M. Myers M.E.M. Chemist: E. Chung

NORMALIZED (ASSUMING AIR FREE)

COMPONENTS	MOLE FRACTION	COMPONENTS	MOLE FRACTION
Methane	0.0457	Methyl-Acetylene	
Ethane	0.0168	cis-2-Butene	
Ethylene		1,3-Butadiene	
Acetylene		i-Pentane	0.0005
Propane	0.0161	n-Pentane	0.0007
Propylene		C_6+	
Propadiene		Carbon Dioxide	
i-Butane	0.0013	Carbon Monoxide	0.0006
n-Butane	0.0120	Hydrogen	0.8987
1-Butene		Nitrogen	0.0073
i-Butylene		Oxygen	
trans-2-Butene		Hydrogen Sulfide	0.0003

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Experiment No. F86-06G **Date:** April 23, 1986

Feedstock: Devco Coal Tar

Catalyst : Sulphided Shell S-424

Reactor Conditions:

1. Temperature: 360°C
2. Pressure: 7.2 MPa
3. Liquid Feed Rate: 25.3 g/hr
4. Hydrogen Rate: 500 cc/min
5. Duration: 2.25 hours

Mass Balance:

Liquid Feed: 57 g
Liquid Product: 64.4 g
Liquid Yield: 113.0 % wt. of fresh feed

Gas Volume: 55 litres (@ 15°C, 1 atm)
Hydrogen Consumption: unable to calculate.
Gas Yield, (Hydrogen free): unable to calculate

Gas Analysis: Experiment stopped before a gas sample could be taken.

Comments: This experiment was stopped after 2.25 hours of operation because a plug in the system was causing unstable operation. The unit operated steadily for almost 2 hours, however, a plug developed causing a high pressure differential in the unit. Attempts to clear the plug were unsuccessful and the experiment was stopped. Initially we had difficulty in determining where the plug was occurring. We determined that the liquid level control valve was plugging causing liquid to be forced through the gas section of the unit. The valve could be plugging with a variety of materials such as unconverted, high boiling material, polymers or ammonium salts (which are common with hydrotreating units).

Experiment No. F86-06H **Date: April 28, 1986**

Feedstock: Devco Coal Tar

Catalyst : Sulphided Shell S-424

Reactor Conditions:

1. Temperature: 360°C
2. Pressure: 6.8 MPa
3. Liquid Feed Rate: 31.25 g/hr
4. Hydrogen Rate: 500 cc/min
5. Duration: 4 hours

Mass Balance:

Liquid Feed: 127 g
Liquid Product: 127.7 g
Liquid Yield: 102.1 % wt.

Gas Volume: 80.7 litres (@ 15°C, 1 atm)
Hydrogen Consumption: .014 g mol/g feed
Gas Yield, (Hydrogen free): 3.4 % wt. fresh feed

Gas Analysis: See following page.

Comments: Identical conditions to F86-06G were used. At this point it was felt the plugging problems were caused by ammonium salt precipitation. The line and valve where the plugging was occurring was insulated and heat traced. The run was unstable throughout with plugging problems. Plugging caused sudden pressure changes which would empty the system more than necessary. A true steady state operation was never achieved. As a consequence it is possible that a significant portion of the material went through the system not fully treated.

With the recurring plugging, we decided that the material was not sufficiently treated or polymers were being formed. We decided to change the order of experiments so that the higher severity conditions would be tested first.

Container Identity	:	Gas Tight Syringe
Experiment No.	:	F86-06H
Originator	:	Doug Soveran
Sample Description	:	Gas Product
Date Received	:	April 28, 1986
Date Reported	:	April 28, 1986

NORMALIZED (Assuming Air Free)

Components	Mole Fraction	Components	Mole Fraction
Methane	.0014	Methyl-Acetylene	
Ethane	.0013	cis-2-Butene	
Ethylene		1,3 Butadiene	
Acetylene		i-Pentane	
Propane	.0018	n-Pentane	
Propylene		C6+	
Propadiene		Carbon Dioxide	.0011
i-Butane		Carbon Monoxide	.0012
n-Butane	.0068	Hydrogen	.9819
1-Butane		Oxygen	.0045
trans-2-Butene		Hydrogen Sulphide	

Experiment No. F86-06I **Date: April 29, 1986**

Feedstock: Devco Coal Tar

Catalyst : Sulphided Shell S-424

Reactor Conditions:

1. Temperature: 380°C
2. Pressure: 10.8 MPa
3. Liquid Feed Rate: 16.75 g/hr
4. Hydrogen Rate: 250 cc/min
5. Duration: 4 hours

Mass Balance:

Liquid Feed: 67 g
Liquid Product: 60.2 g
Liquid Yield: 89.9 % wt. fresh feed

Gas Volume: 22.2 litres (@ 15°C, 1 atm)
Hydrogen Consumption: .025 g mol/g feed
Gas Yield, (Hydrogen free): 5.6 % wt. fresh feed

Gas Analysis: See following page.

Comments: Actually this was the second attempt at these conditions except the pressure for the first attempt was 7 MPa. The unit simply would not operate without plugging occurring. We then increased pressure to minimize polymer formation and tried again.

Thh unit ran smoothly at the higher pressure. No plugging problems occurred in this experiment.

ANALYTICAL REPORT

Container Identity : Gas Tight Syringe
Continuous Unit Run # : F86-06I
Originator : Doug Soveran
Sample Name :
Sample Description : Gas Product
Date Received :
Date Reported : May 02, 1986

A.S. Sample No.: 86-0875
A.S.U. Manager : M. Myers M.E.M. Chemist: E. Chung EC

NORMALIZED (ASSUMING AIR FREE)

COMPONENTS	MOLE FRACTION	COMPONENTS	MOLE FRACTION
Methane	0.0273	Methyl-Acetylene	
Ethane	0.0119	cis-2-Butene	
Ethylene		1,3-Butadiene	
Acetylene		i-Pentane	0.0006
Propane	0.0118	n-Pentane	0.0015
Propylene		C_6+	0.0161
Propadiene		Carbon Dioxide	0.0005
i-Butane	0.0012	Carbon Monoxide	0.0013
n-Butane	0.0136	Hydrogen	0.9089
1-Butene		Nitrogen	0.0036
i-Butylene		Oxygen	
trans-2-Butene		Hydrogen Sulfide	0.0017

Saskatchewan Research Council
PETROLEUM DIVISION
515 Henderson Drive, Regina, Saskatchewan, S4N 5X1, Telephone (306) 787-9329

Experiment No. F86-06J **Date:** April 29, 1986

Feedstock: Devco Coal Tar

Catalyst : Sulphided Shell S-424

Reactor Conditions:

1. Temperature: 360°C
2. Pressure: 10.5 MPa
3. Liquid Feed Rate: 15.25 g/hr
4. Hydrogen Rate: 250 cc/min
5. Duration: 4 hours

Mass Balance:

Liquid Feed: 61 g
Liquid Product: 53.0 g
Liquid Yield: 86.9 % wt. fresh feed

Gas Volume: 39.3 litres (@ 15°C, 1 atm)
Hydrogen Consumption: 0.0165 g mol/g feed
Gas Yield, (Hydrogen free): 14.2 % wt. fresh feed

Gas Analysis: See following page.

Comments: Relatively stable operation, some minor plugging occurred. This indicated that this set of conditions was borderline in preventing the formation the materials causing the plugging or the material was being treated just sufficiently to eliminate the troublesome components.

ANALYTICAL SERVICES LAB

ANALYTICAL REPORT

Container Identity : Gas Tight Syringe
Continuous Unit Run # : F86-06J
Originator : Doug Soveran
Sample Name :
Sample Description : Gas Product
Date Received :
Date Reported : May 02, 1986

A.S. Sample No.: 86-0876
A.S.U. Manager : M. Myers MM Chemist: E. Chung EC

NORMALIZED (ASSUMING AIR FREE)

COMPONENTS	MOLE FRACTION	COMPONENTS	MOLE FRACTION
Methane	0.0088	Methyl-Acetylene	
Ethane	0.0050	cis-2-Butene	
Ethylene		1,3-Butadiene	
Acetylene		i-Pentane	0.0007
Propane	0.0067	n-Pentane	0.0010
Propylene		C_6+	0.0384
Propadiene		Carbon Dioxide	0.0006
i-Butane	0.0019	Carbon Monoxide	0.0017
n-Butane	0.0143	Hydrogen	0.9166
1-Butene		Nitrogen	0.0020
i-Butylene		Oxygen	
trans-2-Butene		Hydrogen Sulfide	0.0023

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GENERAL COMMENTS REGARDING ALL THE EXPERIMENTS

1. Reaction temperature varied significantly aroung the target value. The range was from -2°C to +10°C. This could be attributed to a couple of items. An unsteady feed rate will cause fluctuations in reactor temperature because hydrotreating reactions are quite exothermic. It appeared that we had a steady flow but we cannot be 100% certain. Although the feedstock was heated to 60°C to keep it fluid, it was suspected that the feed was not homogeneous. The feed vessel is not stirred; some components may have settled and periodically drawn into the pump.

2. Hydrogen consumption determinations are very difficult to establish reliably with laboratory units. This is due to a number of reasons. Small leaks in the system are nearly impossible to detect so some losses are inevitable. The accuracy of the mass flowmeters also introduces a significant error. For example, the flow rate for hydrogen is set at 225 cc/min, but the rate is actually 250±25 cc/min. Therefore hydrogen consumption data should be used in a qualitative view rather than a quantitative one.

3. Changes in feedstock quality may have resulted because the feed tank was kept heated at all times during the experimental period. The feed was blanketed with nitrogen but it is impossible to determine if all the oxygen was removed. The feed was kept heated for 7 days; initially this period was to be only 3 days. The plugging problems and an equipment failure extended this period.

4. One additional experiment was planned but we ran out of feedstock just as we were starting it.